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(54) MAGNETIC SUBSTANCE-AMORPHOUS SILICA COMPOSITE PARTICLE AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject composite particles increased in specific surface area and pore volume by neutralizing a granular material of a magnetic substance and a partially neutralized material of an alkali silicate obtained by allowing a mixed solution of silicic acid alkali aqueous solution with magnetic substance particles, a water-soluble polymer and an acid aqueous solution of stand.

SOLUTION: A silicic acid alkali aqueous solution of the formula Na2O.mSiO2.nH2O [(m) is 1-4; (n) is 0 or an arbitrary integer] is mixed with 1-100wt.% (based on SiO2) magnetic substance particles having 0.2-50μm number - average particle diameter (by electron microscope method), 0.1-1.0g/cc apparent density, 1-100 Oe saturated magnetization and 105 to 109Ω.cm volume specific resistance, a water-soluble polymer and an acid aqueous solution to afford a mixed solution having pH10.2-11.2. The mixed solution is allowed to stand at 0-10°C for 1-50hr to deposit a granular material comprising a partially neutralized material of an alkali silicate and a magnetic substance and the granular material is separated and neutralized with an acid to provide the objective magnetic substance-amorphous silica composite particles having 200-800m2/g BET specific surface area, 18-1,000Å pore radius and 0.1-0.6ml/g pore volume.

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CLAIMS

[Claim(s)]

[Claim 1]A magnetic substance amorphous silica composite particle comprising a constituent with 1 thru/or 100% of the weight per SiO_2 of magnetic substance particles distributed in a matrix of amorphous silica, and this matrix.

[Claim 2]The magnetic substance amorphous silica composite particle according to claim 1 in which said composite

particle has the pore volume in 18 thru/or 1000 A of pore radii of a BET specific surface area of 200 thru/or 800-m^2/g, 0.1, or 0.6 mL/g.

[Claim 3]The magnetic substance amorphous silica composite particle according to claim 1 which has the pore volume (macro pore) in 150 thru/or 1000 A of pore radii in the range of 0.01 thru/or 0.4 mL/g.

[Claim 4]The magnetic substance amorphous silica composite particle according to claim 1 in a range whose oil absorption (JIS K5101.21) is 30 thru/or 100 mL(s)/100g.

[Claim 5]The magnetic substance amorphous silica composite particle according to claim 1 which has the number average particle diameter of 0.5 thru/or 50 micrometers by an electron microscope photograph method.

[Claim 6]The magnetic substance amorphous silica composite particle according to claim 1 which has the particle shape near a globular form thru/or a globular form.

[Claim 7]The magnetic substance amorphous silica composite particle according to claim 1 whose magnetic body is a ferrite.

[Claim 8]An acid aqueous solution of alkaline silicate solution, magnetic substance particles, a water-soluble polymer, and the amount of partial neutralization is mixed, A manufacturing method of a magnetic substance amorphous silica composite particle characterized by neutralizing from acid after making granular material which neglects this mixed liquor and comprises a partial neutralized substance and a magnetic body of an alkaline silicate generate and separating this granular material.

[Claim 9]The manufacturing method according to claim 8 which mixes 1 thru/or 100% of the weight of magnetic substance particles on the basis of SiO_2 in an alkaline silicate.

[Claim 10]The manufacturing method according to claim 8 whose viscosity in front of gelling of mixed liquor is 20 or more centipoises.

[Claim 11]The manufacturing method according to claim 8 whose alkaline silicate of the number of 1 thru/or 4 and n is a sodium silicate which has the presentation of ** which is 0 or arbitrary integers in the inside m of a formula, and Na_2O-$mSiO_2$ and a nH_2O type.

[Claim 12]The manufacturing method according to claim 8 whose water-soluble polymer is carboxymethyl cellulose (CMC).

[Claim 13]The manufacturing method according to claim 8 whose acid is sulfuric acid.

[Claim 14]The manufacturing method according to claim 8 which makes alkaline silicate solution distribute magnetic substance particles, mixes these dispersion liquid with a solution of a water-soluble polymer, and finally mixes an acid aqueous solution.

[Claim 15]The manufacturing method according to claim 8 which adds acid on the occasion of partial neutralization so that the pH of mixed liquor may be set to 10.2 thru/or 11.2.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]In this invention, it is related with the manufacturing method of magnetic substance amorphous silica composite particle ****.

Therefore, it is related with the method of manufacturing a magnetic substance amorphous silica composite particle directly in the composite particle and the neutralization process of acid of an alkaline silicate which it changes from the constituent which magnetic substance particles distributed in the matrix of amorphous silica to details more.

[0002]

[Description of the Prior Art]Conventionally, the composite particle of a magnetic body and the nature material of silicic acid is used also for the purpose of giving magnetic adsorptivity to adsorbent and a carrier, as various magnetic materials.

[0003]For example, to JP,60-75330,A. The manufacturing method of the magnetizability zeolite composite introducing each magnetizability particle into the reaction mixture for zeolite generation, and making zeolite generate on the surface of a ferromagnetic particle is indicated, and it is indicated that this thing is useful in a magnetic stabilization fluid bed process.
[0004]In JP,7-235407,A, it has silica gel in the surface and the magnetic particle containing the ferromagnetic which gave the anticorrosion coat to the central part is indicated.
After making this magnetic particle mix or react to a sample, it is indicated that it is efficiently and selectively separable with a sample.

[0005]In JP,5-170425,A, copper of hydrolysis nature, iron, a zirconium, A silica particle is made to distribute uniformly in the solution of the metal salt chosen from aluminum, chromium, and yttrium, and the manufacturing method of the composite particle in which a metallic-compounds enveloping layer is made to form by a hydrolysis reaction subsequently to a silica particle top is indicated.
It is shown that this composite particle is useful as a magnetic material etc.

[0006]
[Problem(s) to be Solved by the Invention]However, there was a problem that the compound state of amorphous silica and a magnetic body is also not necessarily uniform necessarily easily and that it was not uniform to set the ratio of amorphous silica and a magnetic body as the range of early as for these publicly known methods.
[0007]How for this invention persons to add an acrylamide system water soluble polymer as condensation growing agents in the neutralization process by acid of an alkaline silicate in JP,5-193927,A previously, and to manufacture an amorphous silica spherical particle, And although the method of using carboxymethyl cellulose (CMC) for the same method as condensation growing agents was proposed in JP,7-232911,A, In these methods, when magnetic substance particles were distributed in the alkaline silicate, it found out that the magnetic substance amorphous silica composite particle of the new composite construction which magnetic substance particles distributed in the matrix of amorphous silica was obtained.
[0008]Amorphous silica and a magnetic body contain the purpose of this invention by a quantitative ratio suitable for revealing both operation, and are to provide a magnetic substance amorphous silica composite particle which moreover has a new composite construction, and a manufacturing method for the same.
[0009]Other purposes of this invention are to provide a magnetic substance amorphous silica composite particle which has the specific surface area and pore volume which increased as compared with the arithmetic mean value of amorphous silica and a magnetic body, and also also has the macro pore which increased, and a manufacturing method for the same.
[0010]The purpose of further others of this invention is easy to operate, and it is to provide the manufacturing method of the magnetic substance amorphous silica composite particle excellent in productivity.
[0011]
[Means for Solving the Problem]According to this invention, a magnetic substance amorphous silica composite particle comprising a constituent with 1 thru/or 100% of the weight per SiO_2 of magnetic substance particles distributed in a matrix of amorphous silica and this matrix is provided.
[0012]According to this invention, an acid aqueous solution of alkaline silicate solution, magnetic substance particles, a water-soluble polymer, and the amount of partial neutralization is mixed again, After making granular material which neglects this mixed liquor and comprises a partial neutralized substance and a magnetic body of an alkaline silicate generate and separating this granular material, a manufacturing method of a magnetic substance amorphous silica composite particle neutralizing from acid is provided.
[0013]As for a magnetic substance amorphous silica composite particle of this invention, the 1. aforementioned composite particle has the pore volume in 18 thru/or 1000 A of pore radii of a BET specific surface area of 200 thru/or 800-m^2/g, 0.1, or 0.6 mL/g, 2. Pore volume (macro pore) in 150 thru/or 1000 A of pore radii is in the range of 0.01 thru/or 0.4 mL/g, 3. Having the particle shape near it being in a range whose oil absorption (JIS K5101.21) is 30 thru/or

100 mL(s)/100g, having the number average particle diameter of 0.5 thru/or 50 micrometers by 4. electron microscope photograph method, 5. globular form, or a globular form, and being [6. magnetic body / a ferrite] ** are preferred.

[0014]In a manufacturing method of this invention, 1 thru/or 100% of the weight of magnetic substance particles are mixed on the basis of SiO_2 in 1. alkaline silicate, 2. Viscosity in front of gelling of mixed liquor being 20 or more centipoises and 3. alkaline silicate the inside m of a formula, and Na_2O-mSiO_2 and a nH_2O type. The number of 1 thru/or 4 and n being sodium silicates which have the presentation of ** which is 0 or arbitrary integers, and 4. water solubility polymer should be carboxymethyl cellulose (CMC).

5. Adding [so that the pH of mixed liquor may be set to 10.2 thru/or 11.2]-on the occasion of mixing [make that acid is sulfuric acid and 6. alkaline silicate solution distribute magnetic substance particles, mix these dispersion liquid with a solution of a water-soluble polymer, and]-finally-acid aqueous solution and 7. partial neutralization,-acid ** is preferred.

[0015]

[Embodiment of the Invention]In the magnetic substance amorphous silica composite particle of this invention, it is one feature to consist of a matrix of amorphous silica and magnetic substance particles distributed in this matrix. That is, in this composite particle, also in the surface of particles, the inside of particles also has uniform distribution of amorphous silica and magnetic substance particles, and the various characteristics of amorphous silica, for example, adsorptivity, water adsorption nature, a bulking agent function, a carrier function, etc. and the magnetic characteristic as a magnetic body are revealed effectively.

[0016]Drawing 1 and drawing 2 of an accompanying drawing are a scanning electron microscope photograph of the magnetic substance amorphous silica composite particle of this invention, Drawing 1 sees the surface of particles by a reflection electron image, and, on the other hand, that drawing 2 tries (refer to the example mentioned later for details) to be a secondary electron image, Since a difference exceptional in both photograph is not found, in the magnetic substance amorphous silica composite particle of this invention, it is guessed that the inside of a particle and the surface have uniform organization thru/or structure.

[0017]In especially the magnetic substance amorphous silica composite particle of this invention, magnetic substance particles are important also for 1 thru/or 100 % of the weight per SiO_2 existing in 5 thru/or 70% of the weight of quantity in the matrix of amorphous silica. That is, when the quantity of magnetic substance particles is lower than a mentioned range, the magnetic characteristic, for example, the power in which a composite particle is attracted by the magnet, becomes weak, and it is not suitable for the purpose of this invention. On the other hand, if there is more quantity of magnetic substance particles than a mentioned range, it is free for not containing magnetic substance particles in the matrix of amorphous silica, and comes to exist, or moreover, what has small particle diameter comes to be intermingled by indeterminate form particles other than a fixed form particle, and it is inconvenient.

[0018]The magnetic substance amorphous silica composite particle of this invention shows the surprising characteristic that a tendency for pore volume to increase rather as compared with the arithmetic mean of amorphous silica and magnetic substance particles is.

[0019]Drawing 4 sets a horizontal axis as the content of the magnetic substance particles in a constituent, and sets a vertical axis as pore volume, Although the pore volume in 18 thru/or 1000 A of pore radii of a magnetic substance amorphous silica composite particle and the pore volume (macro pore) in 150 thru/or 1000 A of pore radii are plotted, Within the limits of the compounding ratio specified by this invention, it turns out about the pore volume in 150 thru/or 1000 A of pore radii that larger pore volume than an arithmetic mean (straight line of drawing 4) is shown.

[0020]In the magnetic substance amorphous silica composite particle of this invention, in spite of making magnetic substance particles contain, the fall of the characteristics, such as adsorptivity and the support nature of an effective substance, becomes clear [few things] from the above result. In this magnetic substance amorphous silica composite particle, since macro pore is increasing, movement to the adsorption site of a substance and movement from an adsorption site are easy, and excelling also in an adsorption rate or desorption speed is clear.

[0021]In this invention, the acid aqueous solution of alkaline silicate solution, magnetic substance particles, a water-soluble polymer, and the amount of partial neutralization is mixed, After making the granular material which neglects this mixed liquor and comprises the partial neutralized substance and magnetic body of an alkaline silicate generate and separating this granular material, a magnetic substance amorphous silica composite particle is

manufactured by neutralizing from acid.

[0022]Although a water soluble polymer acts as condensation growing agents and the partial neutralized substance of an alkaline silicate is grown up into granular material, i.e., a tufted set thing, in this system of reaction, in the case of this condensation growth, the magnetic substance particles which live together in a system are involved in, and it becomes granular material. In this way, by neutralizing this granular material, amorphous silica serves as a matrix and the composite particle from which magnetic substance particles were distributed over this matrix uniformly and uniformly generates.

[0023][Alkaline silicate] as an alkaline silicate used as a raw material by this invention, m uses the solution of the number of 1 thru/or 4, the alkaline silicate which has the presentation of ** especially whose number of 2.5 thru/or 3.5 and n are 0 or arbitrary integers, especially a sodium silicate among formula Na_2O-mSiO_2 and a nH_2O type. The presentation of this alkaline silicate is related to the stability of mixed liquor, the yield of the granular material to generate, and grain size. If the mole ratio (m) of SiO_2 is smaller than a mentioned range, it becomes difficult to carry out a deposit of partial neutralization particles, and yield falls, particle shape and the shape of particle become irregular easily, and a lot of acid is needed for partial neutralization, and it is not desirable. On the other hand, when the mole ratio of SiO_2 becomes larger than a mentioned range, the stability of mixed liquor falls, it becomes that from which the shape of particle separated from the shape of a real ball, or particle size distribution also has the inconvenience of becoming less sharp etc.

[0024][Magnetic substance particles] Although the magnetic substance particles used for this invention generally comprise magnetic materials publicly known in itself, such as a ferrite, magnetite, or iron powder, its particle-like thing is preferred in respect of dispersibility. A globular shape, the shape of a cube, the infinite form of particle shape, etc. may be arbitrary.

[0025]Generally the particle diameter of magnetic substance particles is expressed with the particle diameter by an electron microscopic method. 0.2 thru/or 50 micrometers of 0.5 thru/or 30-micrometer things are especially preferred.

[0026]Although the density of the appearance of magnetic substance particles is different with a presentation, a surface structure or particle diameter of a magnetic body, etc., generally 0.1 thru/or 1.0g/cc is in the range of 0.2 thru/or 0.8g/cc especially. Especially the saturation magnetization of magnetic substance particles is good for there to be 1 thru/or 100 Oe in the range of 5 thru/or 80Oe.

[0027]As this magnetic powder, the arbitrary things of publicly known magnetic substance powder can be used in itself, for example, a tri-iron tetraoxide (Fe_3O_4) and iron sesquioxide (gamma-Fe_2O_3) etc. -- ferromagnetic iron oxide. Iron oxide zinc ($ZnFe_2O_4$), iron oxide yttrium ($Y_3Fe_5O_{12}$), Cadmium oxide ($CdFe_2O_4$), iron oxide GADORIUMU ($Gd_3Fe_5O_{12}$), Iron oxide copper ($CuFe_2O_4$), iron oxide lead ($PbFe_{12}O_{19}$), Iron oxide neodium ($NdFeO_3$), iron oxide barium ($BaFe_{12}O_{19}$),Ferrites, such as iron oxide manganese ($MnFe_2O_4$), iron oxide lanterns ($LaFeO_3$), or these composites. Or independent or the ferrite which is combination and also contains any one or more sorts of manganese other than the above, zinc, iron, cobalt, nickel, and copper can also use ferromagnetic metal, such as iron powder (Fe), cobalt powder (Co), and nickel powder (nickel), thru/or alloys.

[0028]The thing or the thing of low resistance of high resistance may be sufficient as the electrical resistance of magnetic substance particles, and, generally the thing of 10^5 thru/or 10^9 omega-cm especially 10^7 thru/or 10^8 omega-cm is used for volume resistivity.

[0029][Condensation growing agents] In this invention, a water soluble polymer is used as a condensation growth auxiliary agent. As a water soluble polymer, carboxymethyl cellulose (CMC), starch, Guar gum, locust bean gum, gum arabic, tragacanth gum, Especially CMC is preferred although PURITE issue gum, crystal gum, senega RUGAMU, PVA, MECHIRU cellulose, sodium polyacrylate, polyacrylamide, hydroxyethyl cellulose, methyl cellulose, ethyl cellulose, a polyethylene glycol, etc. are used.

[0030]Carboxymethyl cellulose (referred to as CMC below) is the cellulose ether in which the carboxymethyl group was introduced into the hydroxyl group of cellulose, and is also called cellulose glycolic acid. Although the ranges of the degree of etherification of much CMC marketed although it is also possible to manufacture theoretically CMC of the degree 3 of etherification which etherified all three hydroxyl groups per cellulose unit are 0.5 thru/or 1.0 about, these days, 1.0 or more things are also marketed widely. Generally CMC puts sodium carboxymethyl cellulose (Na-CMC)

which is that sodium salt in many cases, and this thing can be used in favor of the purpose of this invention. The value of the degree of etherification of CMC is a value obtained by the ash alkaline process of CMC industrial meeting issue. That of the degree of etherification using larger carboxymethyl cellulose than 1 as condensation growing agents especially most suitably 0.8 or more 0.5 or more in this invention is preferred. If the viscosity of CMC is influenced by the degree of polymerization of the cellulose molecule which mainly forms CMC as well as water-soluble general polymer and its viscosity is high, What is seldom polymers is preferred, CMC which there is a tendency for a generation deposit of granular material and filtering separation to become difficult, and is used for this invention is expressed with the degree of polymerization described above, and it is good 10 thru/or 3000, and that it is 200 thru/or 1000 preferably.

[0031]In this invention, the above-mentioned water soluble polymer and the condensation growth auxiliary agent which comprises a water-soluble inorganic electrolyte or other water soluble polymers in combination can also be used. As a water-soluble inorganic electrolyte, if it is water solubility and is an inorganic electrolyte which has agglutination to sol etc., can use arbitrary things, but. The mineral acid salt or organic acid salt of the 1st fellows of the periodic table, the 2nd fellows, the 3rd fellows, the 4th group metal, or other transition metals is used, and the suitable example is as follows.

[0032]Mineral acid salt of alkaline metals, such as alkali metal salt, for example, NaCl, and Na_2SO_4; Alkaline earth metal salt, For example, mineral acid salt, such as a calcium chloride, a magnesium chloride, magnesium sulfate, and a calcium nitrate; other water-soluble metal salt, such as zinc chloride, sulfate of zinc, aluminum sulfate, an aluminium chloride, and titanyl sulfate.

[0033]Also among these, alkali metal salt is one of the suitable condensation growth auxiliary agents. It is because the above-mentioned alkali metal salt is effectively recyclable with recycled water solubility polymers by being an ingredient which carries out a byproduction on the occasion of partial neutralization or full neutralization, containing the last granular silica in the separated filtrate, carrying out the reuse of this, and adding into mixed liquor.

[0034]On the other hand, agglutination [as opposed to sol as compared with a univalent metal salt] of polyvalent metallic salt is large, and a condensation growth operation of partial neutralization silica is size in a little addition as compared with univalent metal. Therefore, when mixing of a polyvalent metal kind is permitted, using polyvalent metallic salt is also permitted.

[0035][Acid] Although various inorganic acid and organic acid are used as acid, from the economical standpoint, it is good to use mineral acid, such as sulfuric acid, chloride, nitric acid, and phosphoric acid, and sulfuric acid is most excellent also among these in respect of the yield of granular material, and the uniformity of particle diameter and a gestalt. In order to perform a homogeneous reaction, it is good although using in the form of a dilution-water solution uses it by 1 thru/or 15% of the weight of concentration often and generally. Water-soluble electrolytes, such as NaCl, especially acid salt, and neutral salt may be added to these acid. The quantity of the acid used even if it faces mixing is good for the pH of mixed liquor to use in 10.2 thru/or 11.2, and quantity that is set especially to 10.5 thru/or 11.0 so that partial neutralization may generate a homogeneous mixed solution (it is transparent).

[0036][Mixing and deposit of granular material] In this invention, when the thing which add magnetic substance particles in alkaline silicate solution, and mixes this and to do incorporates magnetic substance particles certainly into the matrix of amorphous silica, it is advantageous. Subsequently, this mixture and a water-soluble polymer are fully mixed. Finally, the mixture of these three ingredients and acid are mixed enough, after making it uniform, this mixed liquor is settled and the granular material of a partial neutralized substance is deposited.

[0037]Generally as this deposit condition, 0 thru/or 100 ** of neglect of 3 thru/or about 20 hours is suitably suitable at the temperature of 10 thru/or 40 ** suitably for 1 thru/or 50 hours. The particle diameter of deposit particles becomes large, so that temperature is generally low, and the particle diameter of deposit particles becomes small, so that temperature is high. It is one of the advantages of this invention that granular material can be controlled by control of temperature in this way. After the particles which separated the depositing particles and mother liquor and carried out re dispersion to water add acid and neutralize, they operate rinsing, desiccation, a classification, etc. and use them as a product. Since undeposited a part for silica and CMC contain in the separated mother liquor or the dispersion liquid after neutralization, these can be reused effective in the following mixed deposit.

[0038]moreover -- accepting necessity -- mixed liquor -- arbitrary silica with detailed particle diameter -- it can also add

beforehand in the quantity mentioned above on the SiO_2 standard per silica full weight by using sol, silica gel, or anhydrous silica powder as a nucleating additive or an extender. As for the silica to be used, it is preferred to have submicron particle diameter.

[0039]Again if needed Titanium other than silica, a zirconium, tin selenium, The sol arbitrary, for example and slurries which are metal particles, such as particles of hydroxide, such as bismuth and antimony, and an oxide especially a submicron particle or nickel, stainless steel, and gold, by adding into mixed liquor. The spherical silica particle by this invention uniformly distributed and included in these particles is obtained.

[0040]silica – although snow textile (product made from Nissan Chemicals) RIYUDOKKUSU etc. are suitably used as a suitable example of sol, the acid silica sol produced by processing an alkaline silicate with mineral acid can also be used.

[0041]the silica of fine particle diameter – as sol thru/or anhydrous silica powder, Aerosil (product made from Japanese Aerosil), fumed silica (made by W. R. Grace), etc. are used suitably. Although primary particle diameter is detailed, since such dry process silica is condensed to the quite large aggregated particle, it is preferred that carry out wet pulverizing and distributed particle diameter uses it as a slurry used as 1 micrometer or less. It is hydrophobicity, and since the silica produced by hydrolyzing organic Silang, for example, trialkoxysilane, also has few particles which primary particle diameter was detailed and condensed, it is suitable for the purpose of giving hydrophobicity.

[0042]In addition, the white titanium pigment which is microscopic particles in comparison, a flower of zinc, pen galla ** iron black, Synthetic Ochre, an aluminosilicate, zeolite, a hydrotalcite, A dawsonite, lithium aluminum carbonate, phyllosilicate, clay, activated alumina, nepheline, titanellow, oxidation chrome green, ultramarine, Prussian blue, calcium carbonate, and the paints particles of carbon black may be added as a nuclear particle.

[0043]In within the limits which does not make the operation as condensation growing agents of CMC other than the above-mentioned mineral constituent check in this invention, Before a silica particle also with spherical organic components, such as a plasticizer, lubricant, a spray for preventing static electricity, an antifogger, an ultraviolet ray absorbent, an infrared absorption agent, an antioxidant, and an antimicrobial agent, grows, it can also add and blend into a system in subsequent arbitrary stages.

[0044]This magnetic body amorphous silica can give coupling agents, such as metallic soap, resin acid soap, various resin or waxes, the Silang system, an alumina system, a titanium system, and a zirconium system, the oxide or hydroxide of various oil and various metal, silica coding, etc. by request.

[0045]The magnetic substance amorphous silica composite particle obtained by this invention is used as a precursor again, On this surface, alkaline-earth metals, such as magnesium, calcium, barium, and strontium, Zinc etc. are made to react with hydroxide, an oxide, an inorganic acid salt, or organic acid salt, and the granular structure of a precursor is maintained, and the layer part of particles can also be denatured to magnetic substance amorphous silica composite particles, such as for example, a phyllo magnesium silicate and a phyllo zinc silicate. Surface character becomes lipophilic property with a metal kind, and this thing is excellent in especially the dispersibility to the inside of resin, and deodorization and a deodorization operation are also accepted. What is necessary is just to use hydroxide of said alkaline-earth metals in the quantity which will be 1 thru/or 20 % of the weight by an oxide basis per whole.

[0046]The magnetic substance amorphous silica composite particle by this invention using these characteristics, Various thermoplastics [not to mention / the resin manufactured using the metallocene catalyst], For example, a crystalline propylene system polymer (the homopolymer or ethylene propylene rubber of propylene), Polyethylene of low -, inside -, high-density, or line low density, an ion bridge construction olefine copolymer, Olefin system resin, such as an ethylene-vinylacetate copolymer and an ethylene-acrylic ester copolymer; Polyethylene terephthalate, Thermoplastic polyester, such as polybutylene terephthalate; 6-nylon, Polyamide resin, such as 6.6-nylon and 6.8-nylon; VCM/PVC, chlorine-containing-resin [, such as a vinylidene chloride,]; – polycarbonate; – it can be used being able to blend with polysulfones, and it can be used in order to give slip characteristics and anti blocking nature especially to resin-molding articles, such as no [various extensions and] extending and a tubular blown film.

[0047]Especially the amorphous silica by this invention can be blended in the quantity of 0.02 thru/or the amount part of duplexs 0.01 thru/or 10 weight sections per thermoplastics 100 weight section to this purpose.

[0048]The amorphous silica by this invention again The extender for various paints and ink, Can blend with adhesives

and a coating resin composition, and can use it for various uses, and can blend as a carrier or a bulking agent to drugs, foodstuffs, agricultural chemicals, an insecticide, etc., and specifically, The carrier for the fluidity improving agent of a toner, high-class abrasive soap, a lusterless filler, and chromatography, It can be used for cosmetics bases, such as a perfume carrier, the bulking agent for putty, adsorbent, a fluidity improving agent, a release agent, the bulking agent for rubbers, a ceramic base, powder foundation, paste state foundation SHIYON, powder, cream, and an antiperspirant, etc.

[0049]

[Example]The following example explains this invention. Physical-properties measurement of the magnetic substance amorphous silica composite particle was based on the following method.

[0050](1) It measured based on chemical composition JIS M-8852 and M-8855.

(2) Sorptomatic Series1800 by the specific surface area by a BET adsorption method, pore volume, and pole diameter CARLO-ERBA was used, and it measured with the BET adsorption method.

(3) It measured using the pore volume automatic mercury pressure ON pore volume measuring device (auto pore 9220 by a microphone ROMERI tex company) by the Hg method.

(4) a particle size Coulter counter (TA-II by a coal tar electronics company) – it measured using aperture tube 100micrometer by law.

(5) 20 typical particles were chosen from the photograph image acquired with the particle diameter scanning electron microscope (Hitachi make S-570) by SEM, the diameter of the particle image was measured using the scale, and the average value was shown as primary particle diameter.

(6) It measured based on oil absorption JIS K-5101-19.

(7) It measured based on bulk-specific-gravity JIS K-6220.

(8) The 9-micrometer-thick polyvinylidene chloride film was wound around the permanent magnet for clerical work with a magnetism examination diameter of 10 mm, and it placed on the sample which accustomed it to the flat surface, and when it raised calmly, the weight of the sample attached to the magnet was measured.

[0051](Example 1) the beaker made from stainless steel of 2L – the marketing No. 3 sodium silicate (SiO_2: – 22.0%) After 165.5 ml of 7.5g balance picking pure water adding ferrite impalpable powder MZF-8081 (made by Sakai Chemical Industry) with the physical properties which show O:7.0% of Na_2, and SiO_2/Na_2 O(mole ratio) = 3.25 in 477 g and Table 1, Agitating with a high stirrer, 375g (CMC/SiO_2=0.15) of 3% solution of carboxymethyl cellulose (degree of polymerization 550 [about]) was added, and it held with a 20 ** thermostat after distribution enough. Subsequently, under churning, in addition (it was pH 10.8 after the end of pouring), churning after the end of pouring was stopped at the speed which carries out the 5% sulfuric acid 475g (H_2SO_4 / Na_2 O= 0.45) beforehand adjusted at 20 ** under whole-quantity notes in about 3 minutes, and it settled at the temperature for 12 hours. In pure water, carry out re dispersion of the cake obtained by adding 99 ml of sulfuric acid after 12-hour settlement, and a ** exception separating settlings and a mother liquor, and enough After distribution, When sulfuric acid was added 5% and pH was mostly stabilized in 3.0 until pH was set to 3.0, it agitated as it is for 1 hour, and it filtered and rinsed after that, a 110 more ** homoiothermal oven ground with the sample mill after desiccation overnight, and the magnetic substance amorphous silica composite particle was obtained (sample 1).

[0052]The size distribution figures according an electron microscope photograph (SEM) to the Coulter counter method to drawing 1 (reflection electron image) and drawing 2 (secondary electron image) were shown in drawing 5 in Table 2 about the chemical composition of this powder, specific surface area, pore volume, a pole diameter, apparent relative density, and a magnetism examination.

[0053](Examples 2-4, comparative example 1) The magnetic substance amorphous silica composite particle was similarly obtained except having changed the quantity of the ferrite impalpable powder of Example 1 into 15.5g, 35g, 60g, and 140g. (Samples 2, 3, 4, and 6) The chemical composition of each powder, specific surface area, pore volume, a pole diameter, apparent relative density, and a magnetism examination were shown in Table 2. About the sample 6, floc magnetic-substance-particles independent [much] other than a magnetic substance amorphous silica composite particle was observed by electron microscope observation.

[0054](Example 5) the beaker made from stainless steel of 2L -- the marketing No. 3 sodium silicate ($SiO_2$21.9% and

Na_2O – 7.1%) After 207.5 ml of 15.5g balance picking pure water adding ferrite impalpable powder MZF-8081 (made by Sakai Chemical Industry) with the physical properties which show SiO_2 / Na_2 O(mole ratio) = 3.19 in 479 g and Table 1, Agitating with a high stirrer, 315g of acrylamide polymer solution (10% solution, average molecular weight 500,000) is added, and is fully distributed. Subsequently, the 5% sulfuric acid 483g beforehand adjusted at 20 ** is added in about 3 minutes (pH after the end of pouring was 10.8), stirring after the end of pouring is stopped, and it is made to settle as it is for 12 hours. In addition, a ** exception carries out [108 ml of sulfuric acid] a stirring part handbill sediment and a mother liquor after 12-hour settlement, If sulfuric acid is added 5% and pH is mostly stabilized in 2.0 until it carries out re dispersion of the obtained cake underwater and pH is enough set to 2.0 after distribution, after stirring as it is for 2 hours, it filters and rinses, and also a cake is repulped, and it is made the spherical-silica-particles slurry of 15% of concentration. Subsequently, a 110 ** homoiothermal dryer ground this cake with the sample mill after desiccation overnight, and the magnetic substance amorphous silica composite particle whose particle diameter is 2-3 micrometers was obtained. (Sample 5)

The chemical composition of this powder, specific surface area, pore volume, a pole diameter, apparent relative density, and a magnetism examination were shown in Table 2.

[0055](Comparative example 2) the beaker made from stainless steel of 2L – the marketing No. 3 sodium silicate (SiO_2 – 22.0%) After 173 ml of 477g balance picking pure water adding SiO_2 / Na_2 O(mole ratio) = 3.25 Na_2O7.0%, Agitating with a high stirrer, 375g of 3% solution of carboxymethyl cellulose (degree of polymerization 550 [about]) was added, and it held with a 20 ** thermostat after distribution enough. Subsequently, the 5% sulfuric acid 475g (H_2SO_4 / Na_2 O= 0.45) beforehand adjusted at 20 ** was slowly added under churning (pH after sulfuric acid pouring was 10.8), churning after the end of pouring was stopped, and it settled at the temperature for 12 hours. In pure water, carry out re dispersion of the cake obtained by in addition a ** exception separating [326 ml of sulfuric acid after 12 hour settlement] settlings and a mother liquor, and enough After distribution, When sulfuric acid was added 5% and pH was mostly stabilized in 3.0 until pH was set to 3.0, it agitated as it is for 1 hour, and it filtered and rinsed after that, a 110 more ** homoiothermal oven ground with the sample mill after desiccation overnight, and particle spherical silica powder was obtained. (Sample 7)

The chemical composition of this powder, specific surface area, pore volume, a pole diameter, apparent relative density, and a magnetism examination were shown in Table 2.

[0056](Comparative example 3) the beaker made from stainless steel of 2L – the marketing No. 3 sodium silicate ($SiO_2$21.9% and Na_2O – 7.1%) SiO_2 / Na_2 O(mole ratio) = 3.19 479g (7% as SiO_2 concentration in total volume) ******, After 223 ml of water adding, adjusting at 20 ** and stirring slowly, 315g of acrylamide polymer solution (10% solution, average molecular weight 500,000) is added, and is fully distributed. Subsequently, the 5% sulfuric acid 483g beforehand adjusted at 20 ** is added in about 3 minutes (pH after the end of pouring was 10.8), stirring after the end of pouring is stopped, and it is made to settle as it is for 12 hours. In addition, a ** exception carries out [108 ml of sulfuric acid after 12 hour settlement] a stirring part handbill sediment and a mother liquor, If sulfuric acid is added 5% and pH is mostly stabilized in 2.0 until it carries out re dispersion of the obtained cake underwater and pH is enough set to 2.0 after distribution, after stirring as it is for 2 hours, it filters and rinses, and also a cake is repulped, and it is made the spherical-silica-particles slurry of 15% of concentration. The magnesium hydroxide powder (Kami-shima #200 made from chemicals) which is equivalent to 20% by MgO conversion to 500g ****** and its solid content in the slurry is added, Enough, after distribution and after having been under hot bath, carrying out heating temperature up to 98 ** and carrying out 8 time processings at the temperature, it filtered and rinsed, and also the sample mill ground after desiccation at 110 **, subsequently it calcinated at 400 ** for 1 hour, and spherical porosity magnesium silicate powder was obtained. (Sample 8)

The chemical composition of this powder, specific surface area, pore volume, a pole diameter, apparent relative density, and a magnetism examination were shown in Table 2.

[0057]

[Table 1]

（フェライト微粉末MZP-8081の物性）

粉末物性（乾燥粉末）

見掛比重	1.31	g/ml
吸油量	37.0	ml/100g
pH	7.8	
比表面積	94.6	m2/g
水分	0.34	%
粒径	0.01	μm
磁力特性		
(粉末) σs	65.7	emu/g
Hc	5.3	エルステッド

Chemical composition (W%)

Fe2O3 MnO ZnO SiO2 Na2O CaO74.8 16.6 8.4 0.012 0.009 0.0017 [0058]

[Table 2]

	実施例					比較例		
試料番号	1	2	3	4	5	6	7	8
化学組成								
Ig-Loss (%)	9.11	9.26	10.5	7.13	9.3	5.25	5.5	10.7
SiO_2 (%)	85.3	74.9	63.5	62.9	76.4	42.2	96.7	67.2
Fe_2O_3 (%)	4.9	11.0	19.0	23.0	10.3	44.0	—	—
Fe_2O_3%/SiO_2	5.7	14.6	29.9	36.5	13.4	04.2	—	—
MgO (%)	—	—	—	—	—	—	—	20.5
BET法								
比表面積 m^2/g	642	453	500	372	521	103	714	630
細孔容積 ml/g	0.63	0.47	0.63	0.55	0.56	0.22	0.7	0.53
細孔径 (Å)	39	41	50	59	43	85	39	33
Hg法								
8～1000(Å)	0.30	0.22	0.28	0.44	0.55	0.37	0.37	0.32
50～1000(Å)	0.04	0.05	0.08	0.16	0.35	0.09	0.05	0.05
見掛比重g/ml	0.61	0.62	0.57	0.48	0.62	0.58	0.54	0.5
吸油量ml/100g	80	66	64	80	66	84	100	104
粒径 (μm)	6.2	4.2	3.8	3.8	5.2	5.5	6.2	5.0
SEM法による粒径 (μm)	4-7	2-4	2-4	2-4	3-5	3-5	4-7	3-5
磁力試験 (g)	0.06	0.12	0.14	0.16	0.12	0.18	0	0

[0059]

[Effect of the Invention]In this invention, acid of alkaline silicate solution, magnetic substance particles, a water-soluble polymer, and the amount of partial neutralization is neutralized after carrying out mixed neglect and separating the granular material to generate.

Therefore, a magnetic substance amorphous silica composite particle is obtained easily, and this composite particle has the feature of consisting of a matrix of amorphous silica, and magnetic substance particles distributed in this matrix. That is, in this composite particle, also in the surface of particles, the inside of particles also has uniform distribution of amorphous silica and magnetic substance particles, and the various characteristics of amorphous silica, for example, adsorptivity, water adsorption nature, a bulking agent function, a carrier function, etc. and the magnetic characteristic as a magnetic body are revealed effectively.

TECHNICAL FIELD

[Industrial Application]In this invention, it is related with the manufacturing method of magnetic substance amorphous silica composite particle ****.
Therefore, it is related with the method of manufacturing a magnetic substance amorphous silica composite particle directly in the composite particle and the neutralization process of acid of an alkaline silicate which it changes from the constituent which magnetic substance particles distributed in the matrix of amorphous silica to details more.

PRIOR ART

[Description of the Prior Art]Conventionally, the composite particle of a magnetic body and the nature material of silicic acid is used also for the purpose of giving magnetic adsorptivity to adsorbent and a carrier, as various magnetic materials.
[0003]For example, to JP,60-75330,A. The manufacturing method of the magnetizability zeolite composite introducing each magnetizability particle into the reaction mixture for zeolite generation, and making zeolite generate on the surface of a ferromagnetic particle is indicated, and it is indicated that this thing is useful in a magnetic stabilization fluid bed process.
[0004]In JP,7-235407,A, it has silica gel in the surface and the magnetic particle containing the ferromagnetic which gave the anticorrosion coat to the central part is indicated.
After making this magnetic particle mix or react to a sample, it is indicated that it is efficiently and selectively separable with a sample.

[0005]In JP,5-170425,A, copper of hydrolysis nature, iron, a zirconium, A silica particle is made to distribute uniformly in the solution of the metal salt chosen from aluminum, chromium, and yttrium, and the manufacturing method of the composite particle in which a metallic-compounds enveloping layer is made to form by a hydrolysis reaction subsequently to a silica particle top is indicated.
It is shown that this composite particle is useful as a magnetic material etc.

EFFECT OF THE INVENTION

[Effect of the Invention]In this invention, acid of alkaline silicate solution, magnetic substance particles, a water-soluble polymer, and the amount of partial neutralization is neutralized after carrying out mixed neglect and separating the granular material to generate.
Therefore, a magnetic substance amorphous silica composite particle is obtained easily, and this composite particle has the feature of consisting of a matrix of amorphous silica, and magnetic substance particles distributed in this matrix. That is, in this composite particle, also in the surface of particles, the inside of particles also has uniform distribution of amorphous silica and magnetic substance particles, and the various characteristics of amorphous silica, for example, adsorptivity, water adsorption nature, a bulking agent function, a carrier function, etc. and the magnetic characteristic as a magnetic body are revealed effectively.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]However, there was a problem that the compound state of amorphous silica and a magnetic body is also not necessarily uniform necessarily easily and that it was not uniform to set the ratio of amorphous silica and a magnetic body as the range of early as for these publicly known methods.
[0007]How for this invention persons to add an acrylamide system water soluble polymer as condensation growing

agents in the neutralization process by acid of an alkaline silicate in JP,5-193927,A previously, and to manufacture an amorphous silica spherical particle, And although the method of using carboxymethyl cellulose (CMC) for the same method as condensation growing agents was proposed in JP,7-232911,A, In these methods, when magnetic substance particles were distributed in the alkaline silicate, it found out that the magnetic substance amorphous silica composite particle of the new composite construction which magnetic substance particles distributed in the matrix of amorphous silica was obtained.

[0008]Amorphous silica and a magnetic body contain the purpose of this invention by a quantitative ratio suitable for revealing both operation, and are to provide a magnetic substance amorphous silica composite particle which moreover has a new composite construction, and a manufacturing method for the same.

[0009]Other purposes of this invention are to provide a magnetic substance amorphous silica composite particle which has the specific surface area and pore volume which increased as compared with the arithmetic mean value of amorphous silica and a magnetic body, and also also has the macro pore which increased, and a manufacturing method for the same.

[0010]The purpose of further others of this invention is easy to operate, and it is to provide the manufacturing method of the magnetic substance amorphous silica composite particle excellent in productivity.

MEANS

[Means for Solving the Problem]According to this invention, a magnetic substance amorphous silica composite particle comprising a constituent with 1 thru/or 100% of the weight per SiO_2 of magnetic substance particles distributed in a matrix of amorphous silica and this matrix is provided.

[0012]According to this invention, an acid aqueous solution of alkaline silicate solution, magnetic substance particles, a water-soluble polymer, and the amount of partial neutralization is mixed again, After making granular material which neglects this mixed liquor and comprises a partial neutralized substance and a magnetic body of an alkaline silicate generate and separating this granular material, a manufacturing method of a magnetic substance amorphous silica composite particle neutralizing from acid is provided.

[0013]As for a magnetic substance amorphous silica composite particle of this invention, the 1. aforementioned composite particle has the pore volume in 18 thru/or 1000 A of pore radii of a BET specific surface area of 200 thru/or 800-m^2/g, 0.1, or 0.6 mL/g, 2. Pore volume (macro pore) in 150 thru/or 1000 A of pore radii is in the range of 0.01 thru/or 0.4 mL/g, 3. Having the particle shape near it being in a range whose oil absorption (JIS K5101.21) is 30 thru/or 100 mL(s)/100g, having the number average particle diameter of 0.5 thru/or 50 micrometers by 4. electron microscope photograph method, 5. globular form, or a globular form, and being [6. magnetic body / a ferrite] ** are preferred.

[0014]In a manufacturing method of this invention, 1 thru/or 100% of the weight of magnetic substance particles are mixed on the basis of SiO_2 in 1. alkaline silicate, 2. Viscosity in front of gelling of mixed liquor being 20 or more centipoises and 3. alkaline silicate the inside m of a formula, and Na_2O-mSiO_2 and a nH_2O type. The number of 1 thru/or 4 and n being sodium silicates which have the presentation of ** which is 0 or arbitrary integers, and 4. water solubility polymer should be carboxymethyl cellulose (CMC).

5. Adding [so that the pH of mixed liquor may be set to 10.2 thru/or 11.2]-on the occasion of mixing [make that acid is sulfuric acid and 6. alkaline silicate solution distribute magnetic substance particles, mix these dispersion liquid with a solution of a water-soluble polymer, and]-finally-acid aqueous solution and 7. partial neutralization,-acid ** is preferred.

[0015]

[Embodiment of the Invention]In the magnetic substance amorphous silica composite particle of this invention, it is one feature to consist of a matrix of amorphous silica and magnetic substance particles distributed in this matrix. That is, in this composite particle, also in the surface of particles, the inside of particles also has uniform distribution of amorphous silica and magnetic substance particles, and the various characteristics of amorphous silica, for example, adsorptivity, water adsorption nature, a bulking agent function, a carrier function, etc. and the magnetic characteristic as a magnetic body are revealed effectively.

[0016]Drawing 1 and drawing 2 of an accompanying drawing are a scanning electron microscope photograph of the magnetic substance amorphous silica composite particle of this invention, Drawing 1 sees the surface of particles by a reflection electron image, and, on the other hand, that drawing 2 tries (refer to the example mentioned later for details) to be a secondary electron image, Since a difference exceptional in both photograph is not found, in the magnetic substance amorphous silica composite particle of this invention, it is guessed that the inside of a particle and the surface have uniform organization thru/or structure.

[0017]In especially the magnetic substance amorphous silica composite particle of this invention, magnetic substance particles are important also for 1 thru/or 100 % of the weight per SiO_2 existing in 5 thru/or 70% of the weight of quantity in the matrix of amorphous silica. That is, when the quantity of magnetic substance particles is lower than a mentioned range, the magnetic characteristic, for example, the power in which a composite particle is attracted by the magnet, becomes weak, and it is not suitable for the purpose of this invention. On the other hand, if there is more quantity of magnetic substance particles than a mentioned range, it is free for not containing magnetic substance particles in the matrix of amorphous silica, and comes to exist, or moreover, what has small particle diameter comes to be intermingled by indeterminate form particles other than a fixed form particle, and it is inconvenient.

[0018]The magnetic substance amorphous silica composite particle of this invention shows the surprising characteristic that a tendency for pore volume to increase rather as compared with the arithmetic mean of amorphous silica and magnetic substance particles is.

[0019]Drawing 4 sets a horizontal axis as the content of the magnetic substance particles in a constituent, and sets a vertical axis as pore volume, Although the pore volume in 18 thru/or 1000 A of pore radii of a magnetic substance amorphous silica composite particle and the pore volume (macro pore) in 150 thru/or 1000 A of pore radii are plotted, Within the limits of the compounding ratio specified by this invention, it turns out about the pore volume in 150 thru/or 1000 A of pore radii that larger pore volume than an arithmetic mean (straight line of drawing 4) is shown.

[0020]In the magnetic substance amorphous silica composite particle of this invention, in spite of making magnetic substance particles contain, the fall of the characteristics, such as adsorptivity and the support nature of an effective substance, becomes clear [few things] from the above result. In this magnetic substance amorphous silica composite particle, since macro pore is increasing, movement to the adsorption site of a substance and movement from an adsorption site are easy, and excelling also in an adsorption rate or desorption speed is clear.

[0021]In this invention, the acid aqueous solution of alkaline silicate solution, magnetic substance particles, a water-soluble polymer, and the amount of partial neutralization is mixed, After making the granular material which neglects this mixed liquor and comprises the partial neutralized substance and magnetic body of an alkaline silicate generate and separating this granular material, a magnetic substance amorphous silica composite particle is manufactured by neutralizing from acid.

[0022]Although a water soluble polymer acts as condensation growing agents and the partial neutralized substance of an alkaline silicate is grown up into granular material, i.e., a tufted set thing, in this system of reaction, in the case of this condensation growth, the magnetic substance particles which live together in a system are involved in, and it becomes granular material. In this way, by neutralizing this granular material, amorphous silica serves as a matrix and the composite particle from which magnetic substance particles were distributed over this matrix uniformly and uniformly generates.

[0023][Alkaline silicate] as an alkaline silicate used as a raw material by this invention, m uses the solution of the number of 1 thru/or 4, the alkaline silicate which has the presentation of ** especially whose number of 2.5 thru/or 3.5 and n are 0 or arbitrary integers, especially a sodium silicate among formula Na_2O-$mSiO_2$ and a nH_2O type. The presentation of this alkaline silicate is related to the stability of mixed liquor, the yield of the granular material to generate, and grain size. If the mole ratio (m) of SiO_2 is smaller than a mentioned range, it becomes difficult to carry out a deposit of partial neutralization particles, and yield falls, particle shape and the shape of particle become irregular easily, and a lot of acid is needed for partial neutralization, and it is not desirable. On the other hand, when the mole ratio of SiO_2 becomes larger than a mentioned range, the stability of mixed liquor falls, it becomes that from which the shape of particle separated from the shape of a real ball, or particle size distribution also has the inconvenience of becoming less sharp etc.

[0024][Magnetic substance particles] Although the magnetic substance particles used for this invention generally comprise magnetic materials publicly known in itself, such as a ferrite, magnetite, or iron powder, its particle-like thing is preferred in respect of dispersibility. A globular shape, the shape of a cube, the infinite form of particle shape, etc. may be arbitrary.

[0025]Generally the particle diameter of magnetic substance particles is expressed with the particle diameter by an electron microscopic method. 0.2 thru/or 50 micrometers of 0.5 thru/or 30-micrometer things are especially preferred.

[0026]Although the density of the appearance of magnetic substance particles is different with a presentation, a surface structure or particle diameter of a magnetic body, etc., generally 0.1 thru/or 1.0g/cc is in the range of 0.2 thru/or 0.8g/cc especially. Especially the saturation magnetization of magnetic substance particles is good for there to be 1 thru/or 100 Oe in the range of 5 thru/or 80Oe.

[0027]As this magnetic powder, the arbitrary things of publicly known magnetic substance powder can be used in itself, for example, a tri-iron tetraoxide (Fe_3O_4) and iron sesquioxide (gamma-Fe $_2O_3$) etc. -- ferromagnetic iron oxide. Iron oxide zinc ($ZnFe_2O_4$), iron oxide yttrium ($Y_3Fe_5O_{12}$), Cadmium oxide ($CdFe_2O_4$), iron oxide GADORIUMU ($Gd_3Fe_5O_{12}$), Iron oxide copper ($CuFe_2O_4$), iron oxide lead ($PbFe_{12}O_{19}$), Iron oxide neodium ($NdFeO_3$), iron oxide barium ($BaFe_{12}O_{19}$),Ferrites, such as iron oxide manganese ($MnFe_2O_4$), iron oxide lanterns ($LaFeO_3$), or these composites. Or independent or the ferrite which is combination and also contains any one or more sorts of manganese other than the above, zinc, iron, cobalt, nickel, and copper can also use ferromagnetic metal, such as iron powder (Fe), cobalt powder (Co), and nickel powder (nickel), thru/or alloys.

[0028]The thing or the thing of low resistance of high resistance may be sufficient as the electrical resistance of magnetic substance particles, and, generally the thing of 10^5 thru/or 10^9 omega-cm especially 10^7 thru/or 10^8 omega-cm is used for volume resistivity.

[0029][Condensation growing agents] In this invention, a water soluble polymer is used as a condensation growth auxiliary agent. As a water soluble polymer, carboxymethyl cellulose (CMC), starch, Guar gum, locust bean gum, gum arabic, tragacanth gum, Especially CMC is preferred although PURITE issue gum, crystal gum, senega RUGAMU, PVA, MECHIRU cellulose, sodium polyacrylate, polyacrylamide, hydroxyethyl cellulose, methyl cellulose, ethyl cellulose, a polyethylene glycol, etc. are used.

[0030]Carboxymethyl cellulose (referred to as CMC below) is the cellulose ether in which the carboxymethyl group was introduced into the hydroxyl group of cellulose, and is also called cellulose glycolic acid. Although the ranges of the degree of etherification of much CMC marketed although it is also possible to manufacture theoretically CMC of the degree 3 of etherification which etherified all three hydroxyl groups per cellulose unit are 0.5 thru/or 1.0 about, these days, 1.0 or more things are also marketed widely. Generally CMC puts sodium carboxymethyl cellulose (Na-CMC) which is that sodium salt in many cases, and this thing can be used in favor of the purpose of this invention. The value of the degree of etherification of CMC is a value obtained by the ash alkaline process of CMC industrial meeting issue. That of the degree of etherification using larger carboxymethyl cellulose than 1 as condensation growing agents especially most suitably 0.8 or more 0.5 or more in this invention is preferred. If the viscosity of CMC is influenced by the degree of polymerization of the cellulose molecule which mainly forms CMC as well as water-soluble general polymer and its viscosity is high, What is seldom polymers is preferred, CMC which there is a tendency for a generation deposit of granular material and filtering separation to become difficult, and is used for this invention is expressed with the degree of polymerization described above, and it is good 10 thru/or 3000, and that it is 200 thru/or 1000 preferably.

[0031]In this invention, the above-mentioned water soluble polymer and the condensation growth auxiliary agent which comprises a water-soluble inorganic electrolyte or other water soluble polymers in combination can also be used. As a water-soluble inorganic electrolyte, if it is water solubility and is an inorganic electrolyte which has agglutination to sol etc., can use arbitrary things, but. The mineral acid salt or organic acid salt of the 1st fellows of the periodic table, the 2nd fellows, the 3rd fellows, the 4th group metal, or other transition metals is used, and the suitable example is as follows.

[0032]Mineral acid salt of alkaline metals, such as alkali metal salt, for example, NaCl, and Na_2SO_4; Alkaline earth metal salt, For example, mineral acid salt, such as a calcium chloride, a magnesium chloride, magnesium sulfate, and a calcium nitrate; other water-soluble metal salt, such as zinc chloride, sulfate of zinc, aluminum sulfate, an aluminium

chloride, and titanyl sulfate.

[0033]Also among these, alkali metal salt is one of the suitable condensation growth auxiliary agents. It is because the above-mentioned alkali metal salt is effectively recyclable with recycled water solubility polymers by being an ingredient which carries out a byproduction on the occasion of partial neutralization or full neutralization, containing the last granular silica in the separated filtrate, carrying out the reuse of this, and adding into mixed liquor.

[0034]On the other hand, agglutination [as opposed to sol as compared with a univalent metal salt] of polyvalent metallic salt is large, and a condensation growth operation of partial neutralization silica is size in a little addition as compared with univalent metal. Therefore, when mixing of a polyvalent metal kind is permitted, using polyvalent metallic salt is also permitted.

[0035][Acid] Although various inorganic acid and organic acid are used as acid, from the economical standpoint, it is good to use mineral acid, such as sulfuric acid, chloride, nitric acid, and phosphoric acid, and sulfuric acid is most excellent also among these in respect of the yield of granular material, and the uniformity of particle diameter and a gestalt. In order to perform a homogeneous reaction, it is good although using in the form of a dilution-water solution uses it by 1 thru/or 15% of the weight of concentration often and generally. Water-soluble electrolytes, such as NaCl, especially acid salt, and neutral salt may be added to these acid. The quantity of the acid used even if it faces mixing is good for the pH of mixed liquor to use in 10.2 thru/or 11.2, and quantity that is set especially to 10.5 thru/or 11.0 so that partial neutralization may generate a homogeneous mixed solution (it is transparent).

[0036][Mixing and deposit of granular material] In this invention, when the thing which add magnetic substance particles in alkaline silicate solution, and mixes this and to do incorporates magnetic substance particles certainly into the matrix of amorphous silica, it is advantageous. Subsequently, this mixture and a water-soluble polymer are fully mixed. Finally, the mixture of these three ingredients and acid are mixed enough, after making it uniform, this mixed liquor is settled and the granular material of a partial neutralized substance is deposited.

[0037]Generally as this deposit condition, 0 thru/or 100 ** of neglect of 3 thru/or about 20 hours is suitably suitable at the temperature of 10 thru/or 40 ** suitably for 1 thru/or 50 hours. The particle diameter of deposit particles becomes large, so that temperature is generally low, and the particle diameter of deposit particles becomes small, so that temperature is high. It is one of the advantages of this invention that granular material can be controlled by control of temperature in this way. After the particles which separated the depositing particles and mother liquor and carried out re dispersion to water add acid and neutralize, they operate rinsing, desiccation, a classification, etc. and use them as a product. Since undeposited a part for silica and CMC contain in the separated mother liquor or the dispersion liquid after neutralization, these can be reused effective in the following mixed deposit.

[0038]moreover -- accepting necessity -- mixed liquor -- arbitrary silica with detailed particle diameter -- it can also add beforehand in the quantity mentioned above on the SiO_2 standard per silica full weight by using sol, silica gel, or anhydrous silica powder as a nucleating additive or an extender. As for the silica to be used, it is preferred to have submicron particle diameter.

[0039]Again if needed Titanium other than silica, a zirconium, tin selenium, The sol arbitrary, for example and slurries which are metal particles, such as particles of hydroxide, such as bismuth and antimony, and an oxide especially a submicron particle or nickel, stainless steel, and gold, by adding into mixed liquor. The spherical silica particle by this invention uniformly distributed and included in these particles is obtained.

[0040]silica -- although snow textile (product made from Nissan Chemicals) RIYUDOKKUSU etc. are suitably used as a suitable example of sol, the acid silica sol produced by processing an alkaline silicate with mineral acid can also be used.

[0041]the silica of fine particle diameter -- as sol thru/or anhydrous silica powder, Aerosil (product made from Japanese Aerosil), fumed silica (made by W. R. Grace), etc. are used suitably. Although primary particle diameter is detailed, since such dry process silica is condensed to the quite large aggregated particle, it is preferred that carry out wet pulverizing and distributed particle diameter uses it as a slurry used as 1 micrometer or less. It is hydrophobicity, and since the silica produced by hydrolyzing organic Silang, for example, trialkoxysilane, also has few particles which primary particle diameter was detailed and condensed, it is suitable for the purpose of giving hydrophobicity.

[0042]In addition, the white titanium pigment which is microscopic particles in comparison, a flower of zinc, pen galla **

iron black, Synthetic Ochre, an aluminosilicate, zeolite, a hydrotalcite, A dawsonite, lithium aluminum carbonate, phyllosilicate, clay, activated alumina, nepheline, titanellow, oxidation chrome green, ultramarine, Prussian blue, calcium carbonate, and the paints particles of carbon black may be added as a nuclear particle.

[0043]In within the limits which does not make the operation as condensation growing agents of CMC other than the above-mentioned mineral constituent check in this invention, Before a silica particle also with spherical organic components, such as a plasticizer, lubricant, a spray for preventing static electricity, an antifogger, an ultraviolet ray absorbent, an infrared absorption agent, an antioxidant, and an antimicrobial agent, grows, it can also add and blend into a system in subsequent arbitrary stages.

[0044]This magnetic body amorphous silica can give coupling agents, such as metallic soap, resin acid soap, various resin or waxes, the Silang system, an alumina system, a titanium system, and a zirconium system, the oxide or hydroxide of various oil and various metal, silica coding, etc. by request.

[0045]The magnetic substance amorphous silica composite particle obtained by this invention is used as a precursor again, On this surface, alkaline-earth metals, such as magnesium, calcium, barium, and strontium, Zinc etc. are made to react with hydroxide, an oxide, an inorganic acid salt, or organic acid salt, and the granular structure of a precursor is maintained, and the layer part of particles can also be denatured to magnetic substance amorphous silica composite particles, such as for example, a phyllo magnesium silicate and a phyllo zinc silicate. Surface character becomes lipophilic property with a metal kind, and this thing is excellent in especially the dispersibility to the inside of resin, and deodorization and a deodorization operation are also accepted. What is necessary is just to use hydroxide of said alkaline-earth metals in the quantity which will be 1 thru/or 20 % of the weight by an oxide basis per whole.

[0046]The magnetic substance amorphous silica composite particle by this invention using these characteristics, Various thermoplastics [not to mention / the resin manufactured using the metallocene catalyst], For example, a crystalline propylene system polymer (the homopolymer or ethylene propylene rubber of propylene), Polyethylene of low -, inside -, high-density, or line low density, an ion bridge construction olefine copolymer, Olefin system resin, such as an ethylene-vinylacetate copolymer and an ethylene-acrylic ester copolymer; Polyethylene terephthalate, Thermoplastic polyester, such as polybutylene terephthalate; 6-nylon, Polyamide resin, such as 6.6-nylon and 6.8-nylon; VCM/PVC, chlorine-containing-resin [, such as a vinylidene chloride,]; -- polycarbonate; -- it can be used being able to blend with polysulfones, and it can be used in order to give slip characteristics and anti blocking nature especially to resin-molding articles, such as no [various extensions and] extending and a tubular blown film.

[0047]Especially the amorphous silica by this invention can be blended in the quantity of 0.02 thru/or the amount part of duplexs 0.01 thru/or 10 weight sections per thermoplastics 100 weight section to this purpose.

[0048]The amorphous silica by this invention again The extender for various paints and ink, Can blend with adhesives and a coating resin composition, and can use it for various uses, and can blend as a carrier or a bulking agent to drugs, foodstuffs, agricultural chemicals, an insecticide, etc., and specifically, The carrier for the fluidity improving agent of a toner, high-class abrasive soap, a lusterless filler, and chromatography, It can be used for cosmetics bases, such as a perfume carrier, the bulking agent for putty, adsorbent, a fluidity improving agent, a release agent, the bulking agent for rubbers, a ceramic base, powder foundation, paste state foundation SHIYON, powder, cream, and an antiperspirant, etc.

EXAMPLE

[Example]The following example explains this invention. Physical-properties measurement of the magnetic substance amorphous silica composite particle was based on the following method.

[0050](1) It measured based on chemical composition JIS M-8852 and M-8855.

(2) Sorptomatic Series1800 by the specific surface area by a BET adsorption method, pore volume, and pole diameter CARLO-ERBA was used, and it measured with the BET adsorption method.

(3) It measured using the pore volume automatic mercury pressure ON pore volume measuring device (auto pore 9220 by a microphone ROMERI tex company) by the Hg method.

(4) a particle size Coulter counter (TA-II by a coal tar electronics company) -- it measured using aperture tube

100micrometer by law.
(5) 20 typical particles were chosen from the photograph image acquired with the particle diameter scanning electron microscope (Hitachi make S-570) by SEM, the diameter of the particle image was measured using the scale, and the average value was shown as primary particle diameter.
(6) It measured based on oil absorption JIS K-5101-19.
(7) It measured based on bulk-specific-gravity JIS K-6220.
(8) The 9-micrometer-thick polyvinylidene chloride film was wound around the permanent magnet for clerical work with a magnetism examination diameter of 10 mm, and it placed on the sample which accustomed it to the flat surface, and when it raised calmly, the weight of the sample attached to the magnet was measured.
[0051](Example 1) the beaker made from stainless steel of 2L -- the marketing No. 3 sodium silicate (SiO_2: -- 22.0%) After 165.5 ml of 7.5g balance picking pure water adding ferrite impalpable powder MZF-8081 (made by Sakai Chemical Industry) with the physical properties which show O:7.0% of Na_2, and SiO_2/Na_2 O(mole ratio) = 3.25 in 477 g and Table 1, Agitating with a high stirrer, 375g (CMC/SiO_2=0.15) of 3% solution of carboxymethyl cellulose (degree of polymerization 550 [about]) was added, and it held with a 20 ** thermostat after distribution enough. Subsequently, under churning, in addition (it was pH 10.8 after the end of pouring), churning after the end of pouring was stopped at the speed which carries out the 5% sulfuric acid 475g (H_2SO_4 / Na_2 O= 0.45) beforehand adjusted at 20 ** under whole-quantity notes in about 3 minutes, and it settled at the temperature for 12 hours. In pure water, carry out re dispersion of the cake obtained by adding 99 ml of sulfuric acid after 12-hour settlement, and a ** exception separating settlings and a mother liquor, and enough After distribution, When sulfuric acid was added 5% and pH was mostly stabilized in 3.0 until pH was set to 3.0, it agitated as it is for 1 hour, and it filtered and rinsed after that, a 110 more ** homoiothermal oven ground with the sample mill after desiccation overnight, and the magnetic substance amorphous silica composite particle was obtained (sample 1).
[0052]The size distribution figures according an electron microscope photograph (SEM) to the Coulter counter method to drawing 1 (reflection electron image) and drawing 2 (secondary electron image) were shown in drawing 5 in Table 2 about the chemical composition of this powder, specific surface area, pore volume, a pole diameter, apparent relative density, and a magnetism examination.
[0053](Examples 2-4, comparative example 1) The magnetic substance amorphous silica composite particle was similarly obtained except having changed the quantity of the ferrite impalpable powder of Example 1 into 15.5g, 35g, 60g, and 140g. (Samples 2, 3, 4, and 6) The chemical composition of each powder, specific surface area, pore volume, a pole diameter, apparent relative density, and a magnetism examination were shown in Table 2. About the sample 6, floc magnetic-substance-particles independent [much] other than a magnetic substance amorphous silica composite particle was observed by electron microscope observation.
[0054](Example 5) the beaker made from stainless steel of 2L -- the marketing No. 3 sodium silicate ($SiO_2$21.9% and Na_2O -- 7.1%) After 207.5 ml of 15.5g balance picking pure water adding ferrite impalpable powder MZF-8081 (made by Sakai Chemical Industry) with the physical properties which show SiO_2 / Na_2 O(mole ratio) = 3.19 in 479 g and Table 1, Agitating with a high stirrer, 315g of acrylamide polymer solution (10% solution, average molecular weight 500,000) is added, and is fully distributed. Subsequently, the 5% sulfuric acid 483g beforehand adjusted at 20 ** is added in about 3 minutes (pH after the end of pouring was 10.8), stirring after the end of pouring is stopped, and it is made to settle as it is for 12 hours. In addition, a ** exception carries out [108 ml of sulfuric acid] a stirring part handbill sediment and a mother liquor after 12-hour settlement, If sulfuric acid is added 5% and pH is mostly stabilized in 2.0 until it carries out re dispersion of the obtained cake underwater and pH is enough set to 2.0 after distribution, after stirring as it is for 2 hours, it filters and rinses, and also a cake is repulped, and it is made the spherical-silica-particles slurry of 15% of concentration. Subsequently, a 110 ** homoiothermal dryer ground this cake with the sample mill after desiccation overnight, and the magnetic substance amorphous silica composite particle whose particle diameter is 2-3 micrometers was obtained. (Sample 5)
The chemical composition of this powder, specific surface area, pore volume, a pole diameter, apparent relative density, and a magnetism examination were shown in Table 2.
[0055](Comparative example 2) the beaker made from stainless steel of 2L -- the marketing No. 3 sodium silicate (SiO_2

– 22.0%) After 173 ml of 477g balance picking pure water adding SiO_2 / Na_2 O(mole ratio) = 3.25 Na_2O7.0%, Agitating with a high stirrer, 375g of 3% solution of carboxymethyl cellulose (degree of polymerization 550 [about]) was added, and it held with a 20 ** thermostat after distribution enough. Subsequently, the 5% sulfuric acid 475g (H_2SO_4 / Na_2 O= 0.45) beforehand adjusted at 20 ** was slowly added under churning (pH after sulfuric acid pouring was 10.8), churning after the end of pouring was stopped, and it settled at the temperature for 12 hours. In pure water, carry out re dispersion of the cake obtained by in addition a ** exception separating [326 ml of sulfuric acid after 12 hour settlement] settlings and a mother liquor, and enough After distribution, When sulfuric acid was added 5% and pH was mostly stabilized in 3.0 until pH was set to 3.0, it agitated as it is for 1 hour, and it filtered and rinsed after that, a 110 more ** homoiothermal oven ground with the sample mill after desiccation overnight, and particle spherical silica powder was obtained. (Sample 7)

The chemical composition of this powder, specific surface area, pore volume, a pole diameter, apparent relative density, and a magnetism examination were shown in Table 2.

[0056](Comparative example 3) the beaker made from stainless steel of 2L – the marketing No. 3 sodium silicate ($SiO_2$21.9% and Na_2O – 7.1%) SiO_2 / Na_2 O(mole ratio) = 3.19 479g (7% as SiO_2 concentration in total volume) ******, After 223 ml of water adding, adjusting at 20 ** and stirring slowly, 315g of acrylamide polymer solution (10% solution, average molecular weight 500,000) is added, and is fully distributed. Subsequently, the 5% sulfuric acid 483g beforehand adjusted at 20 ** is added in about 3 minutes (pH after the end of pouring was 10.8), stirring after the end of pouring is stopped, and it is made to settle as it is for 12 hours. In addition, a ** exception carries out [108 ml of sulfuric acid after 12 hour settlement] a stirring part handbill sediment and a mother liquor, If sulfuric acid is added 5% and pH is mostly stabilized in 2.0 until it carries out re dispersion of the obtained cake underwater and pH is enough set to 2.0 after distribution, after stirring as it is for 2 hours, it filters and rinses, and also a cake is repulped, and it is made the spherical-silica-particles slurry of 15% of concentration. The magnesium hydroxide powder (Kami-shima #200 made from chemicals) which is equivalent to 20% by MgO conversion to 500g ****** and its solid content in the slurry is added, Enough, after distribution and after having been under hot bath, carrying out heating temperature up to 98 ** and carrying out 8 time processings at the temperature, it filtered and rinsed, and also the sample mill ground after desiccation at 110 **, subsequently it calcinated at 400 ** for 1 hour, and spherical porosity magnesium silicate powder was obtained. (Sample 8)

The chemical composition of this powder, specific surface area, pore volume, a pole diameter, apparent relative density, and a magnetism examination were shown in Table 2.

[0057]

[Table 1]

（フェライト微粉末MZF-8081の物性）

粉末物性（乾燥粉末）		
見掛比重	1.31	g/ml
吸油量	37.0	ml/100g
pH	7.8	
比表面積	94.6	m2/g
水分	0.34	%
粒径	0.01	μm
磁力特性		
（粉末） σs	65.7	emu/g
Hc	5.3	ｴﾙｽﾃｯﾄﾞ

Chemical composition (W %)

Fe2O3 MnO ZnO SiO2 Na2O CaO74.8 16.6 8.4 0.012 0.009 0.0017 [0058]

[Table 2]

	実施例					比較例		
試料番号	1	2	3	4	5	6	7	8
化学組成								
Ig-Loss (%)	9.11	9.26	10.5	7.13	9.3	5.25	5.5	10.7
SiO_2 (%)	85.3	74.9	63.5	62.9	76.4	42.2	96.7	67.2
Fe_2O_3 (%)	4.9	11.0	19.0	23.0	10.3	44.0	—	—
Fe_2O_3%/SiO_2	5.7	14.6	29.9	36.5	13.4	04.2	—	—
MgO (%)	—	—	—	—	—	—	—	20.5
BET法								
比表面積 m^2/g	642	453	500	372	521	103	714	630
細孔容積 ml/g	0.63	0.47	0.63	0.55	0.56	0.22	0.7	0.53
細孔径 (Å)	39	41	50	59	43	85	39	33
Hg法								
8～1000(Å)	0.30	0.22	0.28	0.44	0.55	0.37	0.37	0.32
50～1000(Å)	0.04	0.05	0.08	0.16	0.35	0.09	0.05	0.05
見掛比重g/ml	0.61	0.62	0.57	0.48	0.62	0.58	0.54	0.5
吸油量ml/100g	80	66	64	80	66	84	100	104
粒径 (μm)	6.2	4.2	3.8	3.8	5.2	5.5	6.2	5.0
SEM法による粒径 (μm)	4-7	2-4	2-4	2-4	3-5	3-5	4-7	3-5
磁力試験 (g)	0.06	0.12	0.14	0.16	0.12	0.18	0	0

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is an electron microscope photograph in which the X ray reflection electron image of the magnetic substance amorphous silica composite particle obtained in Example 1 is shown (one 5,000 times the magnification of this).

[Drawing 2]It is an electron microscope photograph in which the X ray secondary electron image of the magnetic substance amorphous silica composite particle obtained in Example 1 is shown (one 5,000 times the magnification of this).

[Drawing 3]It is a figure showing the specific surface area of a magnetic substance amorphous silica composite particle and the relation of ferrite content which were obtained in each example.

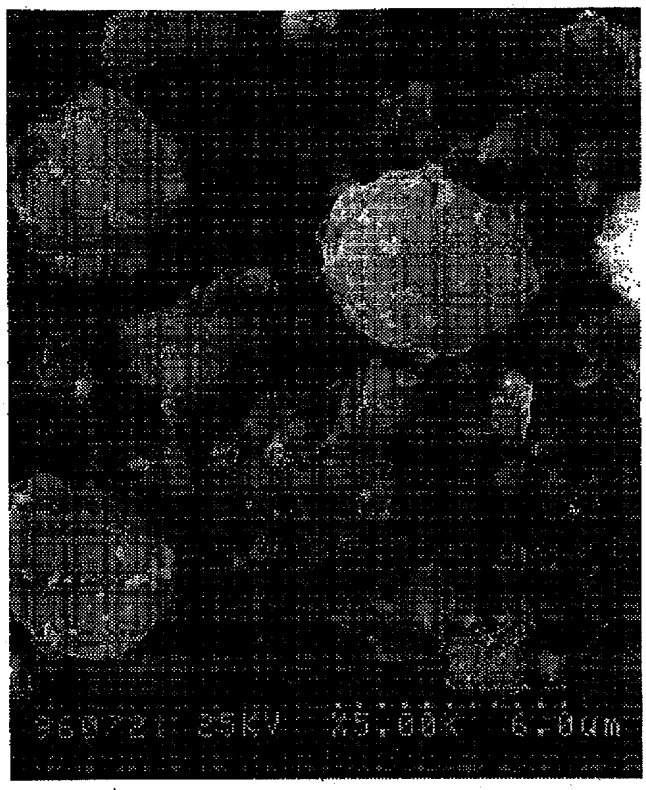
[Drawing 4]It is a figure showing the pore volume of a magnetic substance amorphous silica composite particle and the relation of ferrite content which were obtained in each example.

[Drawing 5]It is the size distribution figures by the Coulter counter method of the magnetic substance amorphous silica composite particle obtained in Example 1.

DRAWINGS

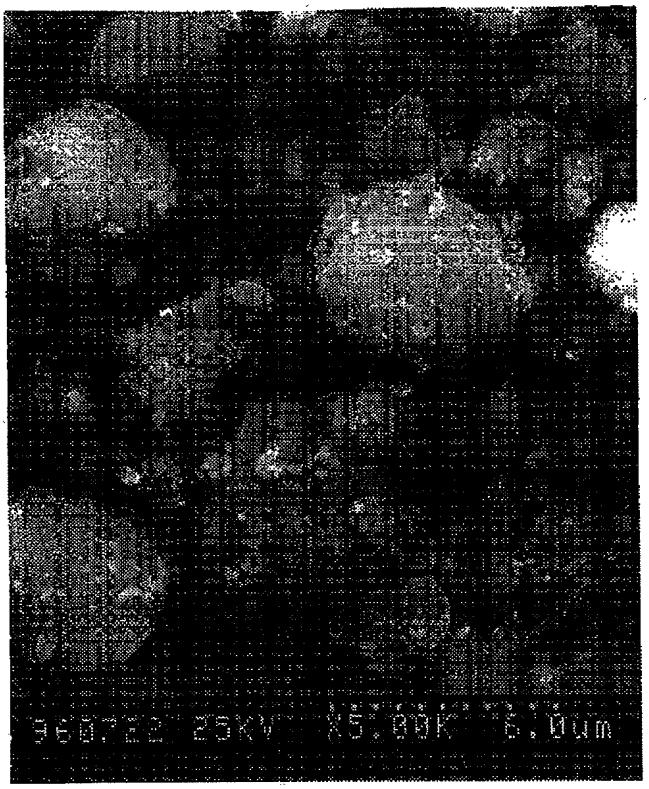
[Drawing 1]

図面代用写真

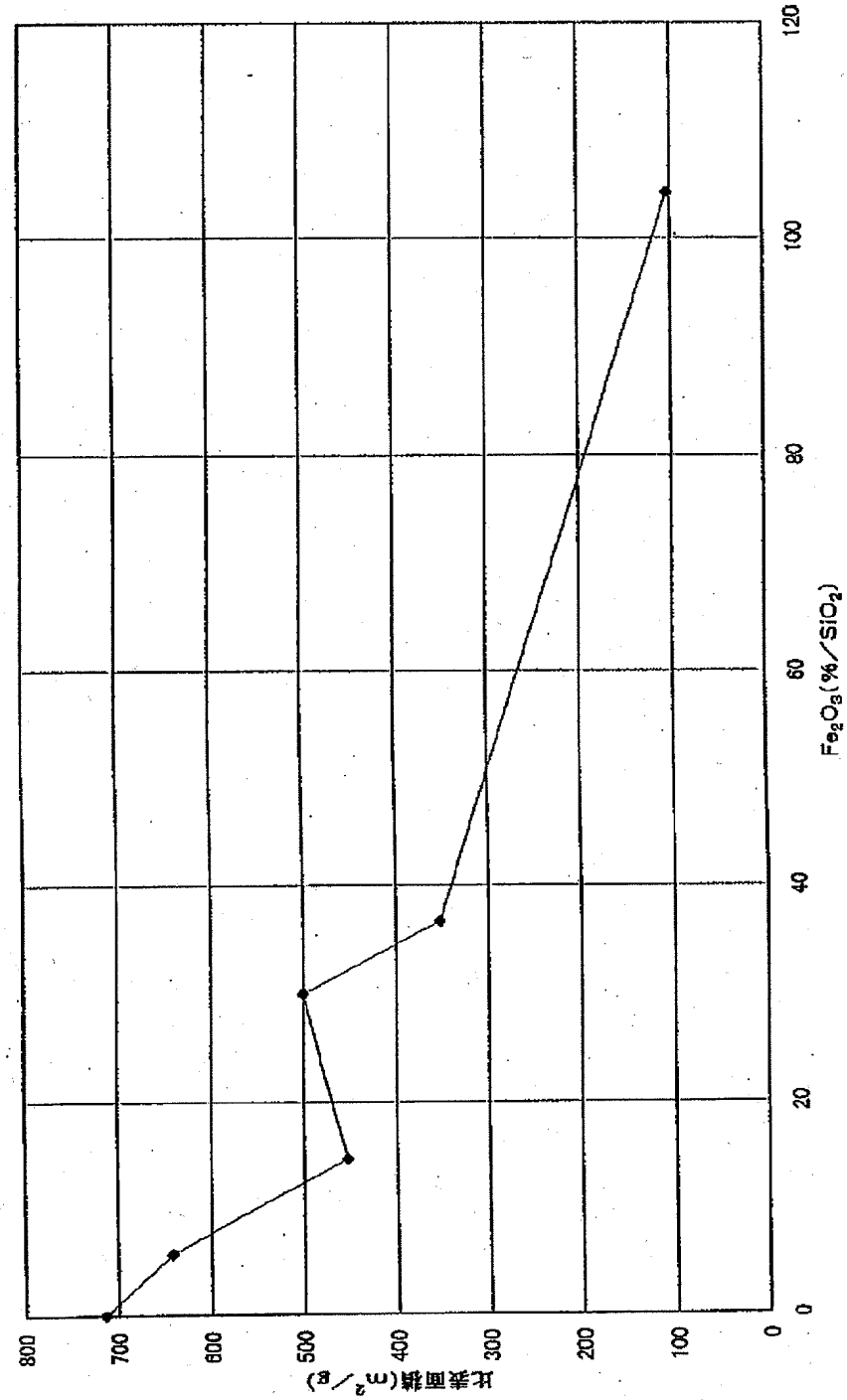


[Drawing 2]

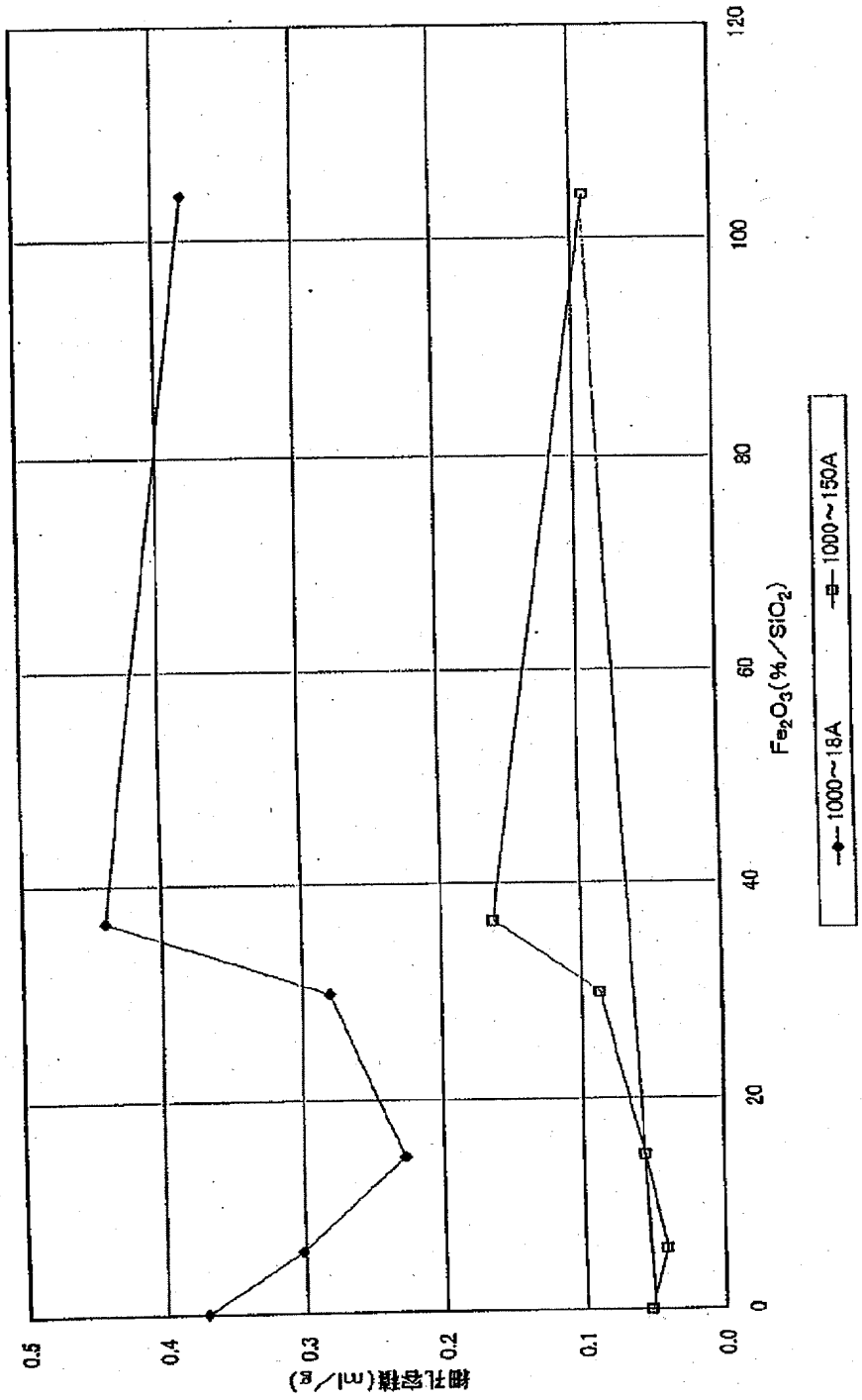
図面代用写真



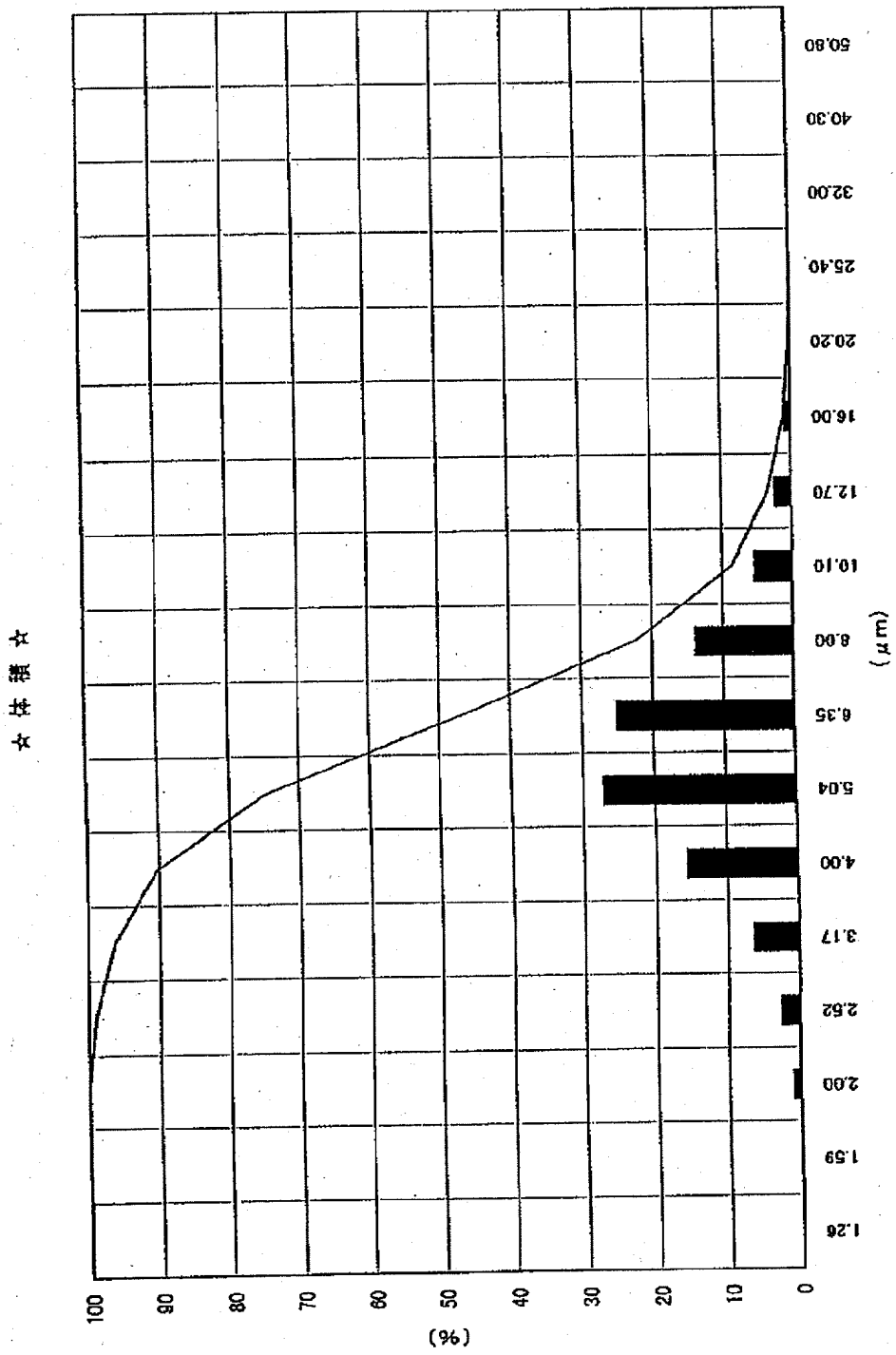
[Drawing 3]


120
100
80
60
40
20
0
Fe_2O_3(%/SiO_2)
800
700
600
500
400
300
200
100
0
比表面積(m^2/g)

[Drawing 4]


細孔容積(ml/g)
0.0
0.1
0.2
0.3
0.4
0.5
Fe_2O_3(%/SiO_2)
0
20
40
60
80
100
120
1000~18A
1000~150A

[Drawing 5]


☆☆☆
50.80
40.30
32.00
25.40
20.20
16.00
12.70
10.10
8.00
6.35
5.04
4.00
3.17
2.62
2.00
1.59
1.26
(μm)
100
90
80
70
60
50
40
30
20
10
0
(%)

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1/22			1/22		

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(54)【発明の名称】　磁性体非晶質シリカ複合粒子及びその製造方法

(57)【要約】

【課題】　非晶質シリカと磁性体とが、両者の作用を発現するのに適した量比で含有され、しかも新規な複合構造を有する磁性体非晶質シリカ複合粒子及びその製造方法を提供する。

【解決手段】　非晶質シリカのマトリックスと該マトリックス中に分散されたSiO_2当たり１乃至１００重量％の磁性体粒子との組成物から成ることを特徴とする磁性体非晶質シリカ複合粒子で、ケイ酸アルカリの酸の中和過程で直接磁性体非晶質シリカ複合粒子を製造する。

【特許請求の範囲】

【請求項１】　非晶質シリカのマトリックスと該マトリックス中に分散されたSiO_2当たり１乃至１００重量％の磁性体粒子との組成物から成ることを特徴とする磁性体非晶質シリカ複合粒子。

【請求項２】　前記複合粒子は２００乃至８００m^2／ｇのＢＥＴ比表面積と０．１乃至０．６ｍＬ／ｇの細孔半径１８乃至１０００オングストロームでの細孔容積とを有する請求項１記載の磁性体非晶質シリカ複合粒子。

【請求項３】　細孔半径１５０乃至１０００オングストロームでの細孔容積（マクロポア）が０．０１乃至０．４ｍＬ／ｇの範囲にある請求項１記載の磁性体非晶質シリカ複合粒子。

【請求項４】　吸油量（ＪＩＳ　Ｋ５１０１．２-１）が３０乃至１００ｍＬ／１００ｇの範囲にある請求項１記載の磁性体非晶質シリカ複合粒子。

【請求項５】　電子顕微鏡写真法で０．５乃至５０μｍの数平均粒径を有する請求項１記載の磁性体非晶質シリカ複合粒子。

【請求項６】　球形乃至球形に近い粒子形状を有する請求項１記載の磁性体非晶質シリカ複合粒子。

【請求項７】　磁性体がフェライトである請求項１記載の磁性体非晶質シリカ複合粒子。

【請求項８】　ケイ酸アルカリ水溶液、磁性体粒子、水溶性重合体及び部分中和量の酸水溶液を混合し、この混合液を放置してケイ酸アルカリの部分中和物と磁性体とから成る粒状物を生成させ、この粒状物を分離した後、酸で中和することを特徴とする磁性体非晶質シリカ複合粒子の製造方法。

【請求項９】　ケイ酸アルカリ中のSiO_2を基準にして１乃至１００重量％の磁性体粒子を混合する請求項８記載の製造方法。

【請求項１０】　混合液のゲル化直前の粘度が２０センチポイズ以上である請求項８記載の製造方法。

【請求項１１】　ケイ酸アルカリが式、

$Na_2O \cdot mSiO_2 \cdot nH_2O$

式中mは、１乃至４の数、nは、０もしくは任意の整数である、の組成を有するケイ酸ナトリウムである請求項８記載の製造方法。

【請求項１２】　水溶性重合体がカルボキシメチルセルロース（ＣＭＣ）である請求項８記載の製造方法。

【請求項１３】　酸が硫酸である請求項８記載の製造方法。

【請求項１４】　ケイ酸アルカリ水溶液に磁性体粒子を分散させ、この分散液を水溶性重合体の溶液と混合し、最後に酸水溶液を混合する請求項８記載の製造方法。

【請求項１５】　部分中和に際して、酸を混合液のｐＨが１０．２乃至１１．２になるように添加する請求項８記載の製造方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、磁性体非晶質シリカ複合粒子及びの製造方法に関するもので、より詳細には、非晶質シリカのマトリックス中に磁性体粒子が分散した組成物から成る複合粒子及びケイ酸アルカリの酸の中和過程で直接磁性体非晶質シリカ複合粒子を製造する方法に関する。

【０００２】

【従来の技術】従来、磁性体とケイ酸質材料との複合粒子は、種々の磁性材料として、また吸着剤や担体に磁気的吸着性を付与する目的にも使用されている。

【０００３】例えば、特開昭６０－７５３３０号公報には、ゼオライト生成用反応混合物中へ個々の磁化性粒子を導入して強磁性粒子の表面上にゼオライトを生成させることを特徴とする磁化性ゼオライト複合材の製造方法が記載され、このものは、磁気的安定化流動床プロセスに有用であることが記載されている。

【０００４】特開平７－２３５４０７号公報には、表面にシリカゲルを持ち、中心部に耐食コートを施した強磁性体を含む磁気粒子が記載されており、この磁気粒子は、試料と混合或いは反応させた後に、効率的に且つ選択的に試料と分離できることが記載されている。

【０００５】特開平５－１７０４２５号公報には、加水分解性の銅、鉄、ジルコニウム、アルミニウム、クロミウム及びイットリウムから選ばれた金属塩の水溶液中にシリカ粒子を均一に分散せしめ、次いで加水分解反応によりシリカ粒子上に金属化合物被覆層を形成させる複合粒子の製造法が記載されており、この複合粒子は、磁性材料等として有用であることが示されている。

【０００６】

【発明が解決しようとする課題】しかしながら、これらの公知の方法は、非晶質シリカと磁性体との比率を初期の範囲に設定することが必ずしも容易でなく、更に非晶質シリカと磁性体との複合状態も必ずしも均一且つ一様でないという問題があった。

【０００７】本発明者らは、先に、特開平５－１９３９２７号公報において、ケイ酸アルカリの酸による中和過程でアクリルアミド系水溶性高分子を凝集成長剤として添加して非晶質シリカ球状粒子を製造する方法、並びに特開平７－２３２９１１号公報において、同様の方法に、凝集成長剤としてカルボキシメチルセルロース（ＣＭＣ）を用いる方法を提案したが、これらの方法において、ケイ酸アルカリ中に磁性体粒子を分散させておくと、非晶質シリカのマトリックス中に磁性体粒子が分散した新規複合構造の磁性体非晶質シリカ複合粒子が得られることを見いだした。

【０００８】本発明の目的は、非晶質シリカと磁性体とが、両者の作用を発現するのに適した量比で含有され、しかも新規な複合構造を有する磁性体非晶質シリカ複合粒子及びその製造方法を提供するにある。

【０００９】本発明の他の目的は、非晶質シリカと磁性体との算術平均値に比して増大した比表面積と細孔容積とを有し、更に増大したマクロポアをも有する磁性体非晶質シリカ複合粒子及びその製造方法を提供するにある。

【００１０】本発明の更に他の目的は、操作が簡単で、生産性に優れた磁性体非晶質シリカ複合粒子の製造方法を提供するにある。

【００１１】

【課題を解決するための手段】本発明によれば、非晶質シリカのマトリックスと該マトリックス中に分散されたSiO_2当たり１乃至１００重量％の磁性体粒子との組成物から成ることを特徴とする磁性体非晶質シリカ複合粒子が提供される。

【００１２】本発明によればまた、ケイ酸アルカリ水溶液、磁性体粒子、水溶性重合体及び部分中和量の酸水溶液を混合し、この混合液を放置してケイ酸アルカリの部分中和物と磁性体とから成る粒状物を生成させ、この粒状物を分離した後、酸で中和することを特徴とする磁性体非晶質シリカ複合粒子の製造方法が提供される。

【００１３】本発明の磁性体非晶質シリカ複合粒子は、

１．前記複合粒子は２００乃至８００m^2／ｇのＢＥＴ比表面積と０．１乃至０．６ｍＬ／ｇの細孔半径１８乃至１０００オングストロームでの細孔容積とを有すること、

２．細孔半径１５０乃至１０００オングストロームでの細孔容積（マクロポア）が０．０１乃至０．４ｍＬ／ｇの範囲にあること、

３．吸油量（ＪＩＳ　Ｋ５１０１．２１）が３０乃至１００ｍＬ／１００ｇの範囲にあること、

４．電子顕微鏡写真法で０．５乃至５０μｍの数平均粒径を有すること、

５．球形乃至球形に近い粒子形状を有すること、

６．磁性体がフェライトであること、

が好ましい。

【００１４】本発明の製造方法においては、

１．ケイ酸アルカリ中のSiO_2を基準にして１乃至１００重量％の磁性体粒子を混合すること、

２．混合液のゲル化直前の粘度が２０センチポイズ以上であること、

３．ケイ酸アルカリが式、

$Na_2O \cdot mSiO_2 \cdot nH_2O$

式中ｍは、１乃至４の数、ｎは、０もしくは任意の整数である、の組成を有するケイ酸ナトリウムであること、

４．水溶性重合体がカルボキシメチルセルロース（ＣＭＣ）であること。

５．酸が硫酸であること、

６．ケイ酸アルカリ水溶液に磁性体粒子を分散させ、この分散液を水溶性重合体の溶液と混合し、最後に酸水溶液を混合すること、

７．部分中和に際して、酸を混合液のｐＨが１０．２乃至１１．２になるように添加すること、が好ましい。

【００１５】

【発明の実施形態】本発明の磁性体非晶質シリカ複合粒子では、非晶質シリカのマトリックスと、このマトリックス中に分散した磁性体粒子とからなることが一つの特徴である。即ち、この複合粒子では、粒子の表面も粒子の内部も、非晶質シリカ及び磁性体粒子の分布が一様であり、非晶質シリカの種々の特性、例えば吸着性、水分吸着性、充填剤機能、担体機能等と、磁性体としての磁気的特性とが有効に発現される。

【００１６】添付図面の図１及び図２は、本発明の磁性体非晶質シリカ複合粒子の走査型電子顕微鏡写真であり、図１は反射電子像で粒子の表面をみたものであり、一方図２は二次電子像でみたものである（詳細は後述する実施例参照）が、両者の写真に格別の相違がみられないことから、本発明の磁性体非晶質シリカ複合粒子では、粒子内部も表面も組織乃至構造が均一であることが推測される。

【００１７】本発明の磁性体非晶質シリカ複合粒子では、磁性体粒子が、非晶質シリカのマトリックス中に、SiO_2当たり１乃至１００重量％、特に５乃至７０重量％の量で存在することも重要である。即ち、磁性体粒子の量が上記範囲よりも低い場合、磁気的特性、例えば複合粒子が磁石に吸引される力が弱くなり、本発明の目的に適さない。一方、磁性体粒子の量が上記範囲よりも多いと、磁性体粒子が非晶質シリカのマトリックスに含まれずにフリーで存在するようになったり、或いは定形粒子以外の不定形粒子でしかも粒径の小さいものが混在するようになって、不都合である。

【００１８】本発明の磁性体非晶質シリカ複合粒子では、細孔容積が、非晶質シリカ及び磁性体粒子の相加平均値に比してむしろ増大する傾向があるという驚くべき特性を示す。

【００１９】図４は、組成物中の磁性体粒子の含有量を横軸とし、細孔容積を縦軸として、磁性体非晶質シリカ複合粒子の細孔半径１８乃至１０００オングストロームでの細孔容積及び細孔半径１５０乃至１０００オングストロームでの細孔容積（マクロポア）をプロットしたものであるが、本発明で規定した配合比の範囲内では、細孔半径１５０乃至１０００オングストロームでの細孔容積については、相加平均値（図４の直線）よりも大きい細孔容積を示していることが分かる。

【００２０】以上の結果から、本発明の磁性体非晶質シリカ複合粒子では、磁性体粒子を含有させているにもかかわらず、吸着性や有効物質の担持性等の特性の低下が少ないことが明らかとなる。また、この磁性体非晶質シリカ複合粒子では、マクロポアが増大しているため、物質の吸着サイトへの移動や吸着サイトからの移動が容易であり、吸着速度や脱着速度にも優れていることが明ら

かである。

【００２１】本発明においては、ケイ酸アルカリ水溶液、磁性体粒子、水溶性重合体及び部分中和量の酸水溶液を混合し、この混合液を放置してケイ酸アルカリの部分中和物と磁性体とから成る粒状物を生成させ、この粒状物を分離した後、酸で中和することにより、磁性体非晶質シリカ複合粒子を製造する。

【００２２】この反応系では、水溶性高分子が凝集成長剤として作用し、ケイ酸アルカリの部分中和物を粒状物、即ち房状集合物に成長させるが、この凝集成長の際、系中に共存する磁性体粒子を巻き込んで粒状物となる。かくして、この粒状物を中和することにより、非晶質シリカがマトリックスとなり、このマトリックスに磁性体粒子が一様且つ均一に分布した複合粒子が生成するのである。

【００２３】［ケイ酸アルカリ］本発明で原料として用いるケイ酸アルカリとしては、式

$Na_2O \cdot mSiO_2 \cdot nH_2O$

式中、mは１乃至４の数、特に２．５乃至３．５の数、nは、０もしくは任意の整数である、の組成を有するケイ酸アルカリ、特にケイ酸ナトリウムの水溶液を使用する。このケイ酸アルカリの組成は、混合液の安定性と生成する粒状物の収率及び粒子サイズとに関係している。SiO_2 のモル比（m）が上記範囲よりも小さいと、部分中和粒子の析出がしにくくなり、収率が低下したり粒子形状や粒子形態が不揃いになり易く、また部分中和に多量の酸が必要になり好ましくない。一方、SiO_2 のモル比が上記範囲よりも大きくなると、混合液の安定性が低下して、粒子形態が真球状から外れたものとなったり、粒径分布もシャープでなくなる等の不都合がある。

【００２４】［磁性体粒子］本発明に用いる磁性体粒子は、一般にフェライト、マグネタイト或いは鉄粉等のそれ自体公知の磁性材料から成るが、微粒子状のものが分散性の点で好ましい。粒子形状は、球状、立方体状、不定形等の任意のものであってよい。

【００２５】磁性体粒子の粒子径は、一般に電子顕微鏡法による粒径で表して　０．２乃至５０μm、特に０．５乃至３０μmのものが好適である。

【００２６】また、磁性体粒子の見掛けの密度は、磁性体の組成や、表面構造或いは粒径等によっても相違するが、一般に０．１乃至１．０ｇ／ｃｃ，特に０．２乃至０．８ｇ／ｃｃの範囲にある。更に、磁性体粒子の飽和磁化は１乃至１０００ｅ、特に５乃至８００ｅの範囲にあるのがよい。

【００２７】この磁性粉としては、それ自体公知の磁性体粉末の任意のものを用いることができ、例えば、四三酸化鉄（Fe_3O_4）、三二酸化鉄（$\gamma-Fe_2O_3$）等の強磁性の鉄酸化物や、酸化鉄亜鉛（$ZnFe_2O_4$）、酸化鉄イットリウム（$Y_3Fe_5O_{12}$）、酸化カドミウム（$CdFe_2O_4$）、酸化鉄ガドリウム（$Gd_3Fe_5O_{12}$）、酸化鉄銅（$CuFe_2O_4$）、酸化鉄鉛（$PbFe_{12}O_{19}$）、酸化鉄ネオジウム（$NdFeO_3$）、酸化鉄バリウム（$BaFe_{12}O_{19}$）、酸化鉄マンガン（$MnFe_2O_4$）、酸化鉄ランタン（$LaFeO_3$）或いはこれらの複合物等のフェライト類、或いは鉄粉（Ｆｅ）、コバルト粉（Ｃｏ）、ニッケル粉（Ｎｉ）等強磁性金属乃至合金類等を単独或いは組み合わせで、更に上記以外のマンガン、亜鉛、鉄、コバルト、ニッケル、銅の何れか１種以上を含むフェライトも用いることができる。

【００２８】磁性体粒子の電気抵抗は、高抵抗のものでも、低抵抗のものでもよく、一般に体積固有抵抗が10^5乃至10^9 Ω・cm、特に10^7乃至10^8 Ω・cmのものが使用される。

【００２９】［凝集成長剤］本発明においては、凝集成長助剤として、水溶性高分子を使用する。水溶性高分子としては、カルボキシメチルセルロース（ＣＭＣ）、澱粉、グアーガム、ローカストビーンガム、アラビヤガム、トラガントガム、プリテイシュガム、クリスタルガム、セネガールガム、ＰＶＡ、メチールセルロース、ポリアクリル酸ソーダ、ポリアクリルアミド、ヒドロキシエチルセルロース、メチルセルロース、エチルセルロース、ポリエチレングリコール等が使用されるが、ＣＭＣが特に好適である。

【００３０】カルボキシメチルセルロース（以下ＣＭＣとすることがある）は、セルロースの水酸基にカルボキシメチル基が導入されたセルロースエーテルであって、セルロースグリコール酸とも呼ばれている。理論的には、セルロース単位当りの３個の水酸基全部をエーテル化したエーテル化度３のＣＭＣを製造することも可能であるが、市販されている多くのＣＭＣのエーテル化度はおおよそ０．５乃至１．０の範囲であるが、最近では１．０以上のものも広く市販されている。一般に、ＣＭＣとはそのナトリウム塩であるナトリウムカルボキシメチルセルロース（Ｎａ－ＣＭＣ）をさす場合が多く、このものは本発明の目的に有利に使用できる。なおＣＭＣのエーテル化度の値は、ＣＭＣ工業会発行の灰分アルカリ法により得られた値である。本発明では、エーテル化度が０．５以上、特に０．８以上、最も好適には１よりも大きいカルボキシメチルセルロースを凝集成長剤として使用することのが好適である。また、ＣＭＣの粘度は、一般の水溶性ポリマーと同じく、主にＣＭＣを形成するセルロース分子の重合度に左右され、粘度が高いと、粒状物の生成析出、濾過分離が困難となる傾向があり、本発明に用いるＣＭＣはあまり高分子でないものが好ましく、上記する重合度で表して１０乃至３０００、好ましくは２００乃至１０００であるのがよい。

【００３１】本発明では、上記水溶性高分子と組み合わせで、水溶性無機電解質或いは他の水溶性高分子から成る凝集成長助剤を使用することもできる。水溶性無機電

解質としては、水溶性であって、ゾル等に対して凝集作用を有する無機の電解質であれば任意のものを使用することができるが、周期律表第１族、第２族、第３族、第４族金属或いは他の遷移金属の鉱酸塩或いは有機酸塩が使用され、その適当な例は次の通りである。

【００３２】アルカリ金属塩、例えばＮａＣｌ、Na_2SO_4等のアルカリ金属の鉱酸塩；アルカリ土類金属塩、例えば塩化カルシウム、塩化マグネシウム、硫酸マグネシウム、硝酸カルシウム等の鉱酸塩；塩化亜鉛、硫酸亜鉛、硫酸アルミニウム、塩化アルミニウム、硫酸チタニル等の他の水溶性金属塩。

【００３３】これらの内でも、アルカリ金属塩は好適な凝集成長助剤の一つである。というのは、上記アルカリ金属塩は部分中和や完全中和に際して副生する成分であり、最終粒状シリカを分離した濾液中に含有されており、これを再使用して混合液に添加することにより、回収水溶性高分子とともに有効に再利用できるからである。

【００３４】一方、多価金属塩は１価金属塩に比してゾルに対する凝集作用が大きく、１価金属に比して少量の添加で部分中和シリカの凝集成長作用が大である。従って、多価金属種の混入が許容される場合には、多価金属塩を使用することも許容される。

【００３５】［酸］酸としては、種々の無機酸や有機酸が使用されるが、経済的見地からは、硫酸、塩酸、硝酸、リン酸等の鉱酸を用いるのがよく、これらの内でも、粒状物の収率や、粒径及び形態の一様さの点で硫酸が最も優れている。均質な反応を行うためには、希釈水溶液の形で用いるのがよく、一般に１乃至１５重量％の濃度で使用するがよい。更にこれらの酸にはＮａＣｌ等の水溶性電解質、特に酸性塩、中性塩を加えておいても良い。混合に際しても使用する酸の量は部分中和により均質な混合溶液（透明である）を生成するようなものであり、混合液のｐＨが１０．２乃至１１．２、特に１０．５乃至１１．０となるような量で用いるのがよい。

【００３６】［混合及び粒状物の析出］本発明において、ケイ酸アルカリ水溶液に磁性体粒子を添加し、これを混合するすることが、磁性体粒子を非晶質シリカのマトリックス中に確実に取り込む上で有利である。次いで、この混合物と水溶性重合体とを十分に混合する。最後に、これら３成分の混合物と酸とを十分混合して、均質化させた後、この混合液を静置して部分中和物の粒状物を析出させる。

【００３７】この析出条件としては、一般に０乃至１００℃好適には１０乃至４０℃の温度で１乃至５０時間、好適には３乃至２０時間程度の放置が適している。一般に温度が低い程、析出粒子の粒径が大きくなり、温度が高い程析出粒子の粒径が小さくなる。かくして温度の制御により、粒状物を制御しうることが本発明の利点の一つである。析出した粒子と母液とを分離し、水に再分散した粒子は、酸を加え中和した後、水洗、乾燥、分級等の操作を行って製品とする。分離した母液や中和後の分散液には未析出のシリカ分や、ＣＭＣが含有されているので、これらは次の混合析出に有効に再利用できることになる。

【００３８】また必要に応じて、混合液に、粒径が微細な任意のシリカゾル、シリカゲルまたは無水シリカ粉末を核剤或いは増量剤として、シリカ全重量当りSiO_2基準で前述した量で予め添加しておくことも出来る。用いるシリカはサブミクロンの粒径を有することが好ましい。

【００３９】更にまた必要に応じて、シリカ以外のチタニウム、ジルコニウム、錫セレン、ビスマス、アンチモン等の水酸化物及び酸化物の微粒子、特にサブミクロン粒子又はニッケル、ステンレス、金等の金属微粒子である例えば任意のゾル及びスラリーを混合液に添加しておくことで、これらの粒子を均一に分散、包含された本発明による球状のシリカ粒子が得られる。

【００４０】シリカゾルの適当な例としては、スノーテックス（日産化学（株）製）リユドックス等が好適に使用されるが、ケイ酸アルカリを鉱酸で処理して得られる酸性シリカゾルを用いることも出来る。

【００４１】微小粒径のシリカゾル乃至無水シリカ粉末としては、アエロジル（日本アエロジル（株）製）、ヒュームドシリカ（Ｗ・Ｒ・グレース製）等が好適に使用される。これらの乾式法シリカは、一次粒子径は微細であるが、かなり大きい二次粒子に凝集しているので、湿式微粉砕し、分散粒径が１μｍ以下となったスラリーとして使用することが好ましい。有機シラン、例えばトリアルコキシシラン類を加水分解して得られるシリカは、疎水性であり、一次粒子径が微細で凝集した粒子も少ないため、疎水性を付与する目的には好適なものである。

【００４２】その他、比較的に微細粒子であるチタン白、亜鉛華、ベンガラ、鉄黒、黄色酸化鉄、アルミノケイ酸塩、ゼオライト、ハイドロタルサイト、ドーソナイト、リチウムアルミニウムカーボネート、フィロケイ酸塩、白土、活性アルミナ、ネフェリン、チタンエロー、酸化クロムグリーン、群青、紺青、炭カル、カーボンブラックの顔料粒子を核粒子として添加してもよい。

【００４３】また本発明においては、上記した無機成分の他に、ＣＭＣの凝集成長剤としての作用を阻害させない範囲内において、可塑剤、滑剤、帯電防止剤、防曇剤、紫外線吸収剤、赤外線吸収剤、酸化防止剤、抗菌剤等の有機成分も球状のシリカ粒子が成長する前或いはその後の任意の段階で系中に添加し配合することもできる。

【００４４】また、この磁性体非晶質シリカは、金属石鹸、樹脂酸石鹸、各種樹脂乃至ワックス類、シラン系、アルミナ系、チタン系、ジルコニウム系等のカップリング剤や各種オイル、各種金属の酸化物もしくは水酸化物

やシリカコーティング等を所望により施すことができる。

【００４５】更にまた、本発明で得られる磁性体非晶質シリカ複合粒子を前駆体として、この表面にマグネシウム、カルシウム、バリウム、ストロンチウム等のアルカリ土類金属、亜鉛等を水酸化物、酸化物又は無機酸塩或いは有機酸塩で反応させて、前駆体の粒状構造が維持され且つ粒子の表層部を例えばフィロケイ酸マグネシウム、フィロケイ酸亜鉛等のような磁性体非晶質シリカ複合粒子に変性させることも出来る。このものは、金属種により表面の性質が親油性になり、樹脂中への分散性に特に優れており、また脱臭、消臭作用も認められる。前記アルカリ土類金属の水酸化物等は、全体当たり酸化物基準で１乃至２０重量％となる量で使用すればよい。

【００４６】これらの特性を利用して、本発明による磁性体非晶質シリカ複合粒子は、メタロセン触媒を用いて製造した樹脂はもちろんのこと、種々の熱可塑性樹脂、例えば結晶性プロピレン系重合体（プロピレンのホモポリマー又はエチレン－プロピレン共重合体）、低－、中－、高－密度の或いは線状低密度のポリエチレン、イオン架橋オレフィン共重合体、エチレン－酢酸ビニル共重合体、エチレン－アクリル酸エステル共重合体等のオレフィン系樹脂；ポリエチレンテレフタレート、ポリブチレンテレフタレート等の熱可塑性ポリエステル；６－ナイロン、６．６－ナイロン、６．８－ナイロン等のポリアミド樹脂；塩化ビニル、塩化ビニリデン等の塩素含有樹脂；ポリカーボネート；ポリスルホン類等に配合して使用することができ、特に各種延伸、無延伸、インフレーションフィルム等の樹脂成形品に、スリップ性、アンチブロッキング性を与えるために使用することができる。

【００４７】この目的に対して、本発明による非晶質シリカは熱可塑性樹脂１００重量部当り０．０１乃至１０重量部、特に０．０２乃至２重量部の量で配合することが出来る。

【００４８】更にまた、本発明による非晶質シリカは、各種塗料、インク用体質顔料、接着剤、コーティング樹脂組成物に配合して種々の用途に使用する事ができ、また医薬品、食品、農薬、殺虫剤等に対して担体や充填剤として配合することができ、具体的には、トナーの流動性改良剤、高級研磨剤、艶消しフィラー、クロマト用担体、香料担体、パテ用充填剤、吸着剤、流動性改良剤、離型剤、ゴム用充填剤、セラミックス基剤、パウダーファンデーション、ペースト状ファンデシーョン、ベビーパウダー、クリーム、制汗剤等の化粧料基剤等に使用できる。

【００４９】

【実施例】本発明を次の実施例で説明する。尚、磁性体非晶質シリカ複合粒子の物性測定は次の方法によった。

【００５０】（１）化学組成

ＪＩＳ　Ｍ－８８５２、Ｍ－８８５５に準拠して測定した。

（２）ＢＥＴ法による比表面積、細孔容積、細孔径

CARLO-ERBA社製Sorptomatic Series1800を使用し、ＢＥＴ法により測定した。

（３）Ｈｇ法による細孔容積

自動水銀圧入細孔容積測定装置（ﾏｲｸﾛﾒﾘﾃｸｽ社製ｵｰﾄﾎﾟｱ9220）を用いて測定した。

（４）粒度

コールターカウンター（コールターエレクトロニクス社製ＴＡ－II）法によりアパチャーチューブ１００μｍを用いて測定した。

（５）ＳＥＭによる粒径

走査型電子顕微鏡（日立製Ｓ－５７０）で得られた写真像から、代表的な粒子２０個を選んで、スケールを用いて粒子像の直径を測定しその平均値を一次粒子径として示した。

（６）吸油量

ＪＩＳ　Ｋ－５１０１－１９に準拠して測定した。

（７）見掛比重

ＪＩＳ　Ｋ－６２２０に準拠して測定した。

（８）磁力試験

直径１０ｍｍの事務用永久磁石に厚さ９μｍのポリ塩化ビニリデンフィルムを巻き、それを平面にならした試料上に置き、静かに持ち上げたときに磁石に付いた試料の重量を測定した。

【００５１】（実施例１）２Ｌのステンレス製ビーカーに市販３号珪酸ソーダ（SiO_2：２２．０％、Na_2O：７．０％、SiO_2／Na_2O（モル比）＝３．２５）を４７７ｇと表１に示す物性を持つフェライト微粉末MZF-8081（堺化学工業製）を７．５ｇ秤取り純水１６５．５ｍｌ加えた後、ハイスターラーで撹拌しながらカルボキシメチルセルロース（重合度約５５０）の３％水溶液を３７５ｇ（ＣＭＣ／SiO_2＝０．１５）加え十分分散後２０℃の恒温槽で保持した。次いで撹拌下にあらかじめ２０℃に調節した５％硫酸４７５ｇ（H_2SO_4／Na_2O＝０．４５）を約３分間で全量注下する速度で加え（注加終了後のｐＨ１０．８であった）、注加終了後撹拌を止めその温度で１２時間静置した。１２時間静置後硫酸９９ｍｌを加え、沈澱物と母液を濾別分離し、得られたケーキを純水中で再分散し十分分散後、ｐＨが３．０になるまで５％硫酸を加え、ｐＨが３．０でほぼ安定したらそのまま１時間撹拌し、以後濾過、水洗し、さらに１１０℃の恒温乾燥器で一夜乾燥後、サンプルミルで粉砕し、磁性体非晶質シリカ複合粒子を得た（試料１）。

【００５２】この粉末の化学組成、比表面積、細孔容積、細孔径、見掛け比重、磁力試験について表２に、電子顕微鏡写真（ＳＥＭ）を図１（反射電子像）及び図２（二次電子像）に、コールターカウンター法による粒度

分布図を図５に示した。

【００５３】（実施例２～４、比較例１）実施例１のフェライト微粉末の量を１５．５g、３５g、６０g、１４０gに変えた以外は同様にして磁性体非晶質シリカ複合粒子を得た。（試料２，３，４，６）各粉末の化学組成、比表面積、細孔容積、細孔径、見掛け比重、磁力試験について表２に示した。試料６については電子顕微鏡観察により磁性体非晶質シリカ複合粒子の他に多数の磁性体粒子単独の凝集粒子が観測された。

【００５４】（実施例５）２Ｌのステンレス製ビーカーに市販３号ケイ酸ソーダ（SiO_2 ２１．９%，Na_2O ７．１%、SiO_2／Na_2O（モル比）＝３．１９）を４７９ｇと表１に示す物性を持つフェライト微粉末MZF-8081（堺化学工業製）を１５．５ｇ秤取り純水２０７．５ｍｌ加えた後、ハイスターラーで撹拌しながらアクリルアミドポリマー水溶液（１０%水溶液、平均分子量５０万）を３１５ｇ加えて十分に分散させる。次いで、予め２０℃に調節した５%硫酸４８３ｇを約３分間で加え（注加終了後のｐＨは１０．８であった）、注加終了後撹拌を止め、そのまま１２時間静置させる。１２時間静置後、硫酸１０８ｍｌ加え撹拌分散し沈殿物と母液を濾別し、得られたケーキを水中で再分散し十分分散後、ｐＨが２．０になるまで５%硫酸を加え、ｐＨが２．０でほぼ安定したら、そのまま２時間撹拌した後、濾過・水洗し、更にケーキをリパルプし、濃度１５%の球状シリカ粒子スラリーにする。次いで、このケーキを１１０℃の恒温乾燥機で一夜乾燥後、サンプルミルで粉砕し、粒子径が２～３μmの磁性体非晶質シリカ複合粒子を得た。（試料５）

この粉末の化学組成、比表面積、細孔容積、細孔径、見掛け比重、磁力試験について表２に示した。

【００５５】（比較例２）２Ｌのステンレス製ビーカーに市販３号珪酸ソーダ（SiO_2 ２２．０%、Na_2O ７．０%、SiO_2／Na_2O（モル比）＝３．２５）を４７７ｇ秤取り純水１７３ｍｌ加えた後、ハイスターラーで撹拌しながらカルボキシメチルセルロース（重合度約５５０）の３%水溶液を３７５ｇ加え十分分散後２０℃の恒温槽で保持した。次いで撹拌下にあらかじめ２０℃に調節した５%硫酸４７５ｇ（H_2SO_4／Na_2O＝０．４５）をゆっくり加え（硫酸注加後のｐＨは１０．８であった）、注加終了後撹拌を止めその温度で１２時間静置した。１２時間静置後硫酸３２６ｍｌ加え沈澱物と母液を濾別分離し、得られたケーキを純水中で再分散し十分分散後、ｐＨが３．０になるまで５%硫酸を加え、ｐＨが３．０でほぼ安定したらそのまま１時間撹拌し、以後濾過、水洗し、さらに１１０℃の恒温乾燥器で一夜乾燥後、サンプルミルで粉砕し、微粒子球状シリカ粉末を得た。（試料７）

この粉末の化学組成、比表面積、細孔容積、細孔径、見掛け比重、磁力試験について表２に示した。

【００５６】（比較例３）２Ｌのステンレス製ビーカーに市販３号ケイ酸ソーダ（SiO_2 ２１．９%，Na_2O ７．１%、SiO_2／Na_2O（モル比）＝３．１９）を４７９ｇ（全液量中のSiO_2 濃度として７%）秤採り、水２２３ｍｌ加えた後、２０℃に調節し、ゆっくり撹拌しながらアクリルアミドポリマー水溶液（１０%水溶液、平均分子量５０万）を３１５ｇ加えて十分に分散させる。次いで、予め２０℃に調節した５%硫酸４８３ｇを約３分間で加え（注加終了後のｐＨは１０．８であった）、注加終了後撹拌を止め、そのまま１２時間静置させる。１２時間静置後硫酸１０８ｍｌ加え、撹拌分散し沈殿物と母液を濾別し、得られたケーキを水中で再分散し十分分散後、ｐＨが２．０になるまで５%硫酸を加え、ｐＨが２．０でほぼ安定したら、そのまま２時間撹拌した後、濾過・水洗し、更にケーキをリパルプし、濃度１５%の球状シリカ粒子スラリーにする。そのスラリーを５００ｇ秤採り、その固形分に対し、ＭｇＯ換算で２０%に相当する水酸化マグネシウム粉末（神島化学製＃２００）を加え、十分分散後、温浴中で９８℃まで加熱昇温し、その温度で８時間処理した後、濾過、水洗し、更に１１０℃で乾燥後、サンプルミルで粉砕し、次いで４００℃で１時間焼成して球状の多孔質ケイ酸マグネシウム粉末を得た。（試料８）

この粉末の化学組成、比表面積、細孔容積、細孔径、見掛け比重、磁力試験について表２に示した。

【００５７】

【表１】

（フェライト微粉末MZF-8081の物性）

粉末物性（乾燥粉末）		
見掛比重	**1.31**	**g/ml**
吸油量	**37.0**	**ml/100g**
pH	**7.8**	
比表面積	**94.6**	**m2/g**
水分	**0.34**	**%**
粒径	**0.01**	**μm**
磁力特性		
(粉末)　σs	**65.7**	**emu/g**
Hc	**5.3**	**ｴﾙｽﾃｯﾄﾞ**

化学組成（W%）

Fe2O3	MnO	ZnO	SiO2	Na2O	CaO
74.8	16.6	8.4	0.012	0.009	0.0017

【００５８】

【表２】

	実施例					比較例		
試料番号	1	2	3	4	5	6	7	8
化学組成								
Ig-Loss (%)	9.11	9.26	10.5	7.13	9.3	5.25	5.5	10.7
SiO_2 (%)	85.3	74.9	63.5	62.9	76.4	42.2	96.7	67.2
Fe_2O_3 (%)	4.9	11.0	19.0	23.0	10.3	44.0	—	—
Fe_2O_3%/SiO_2	5.7	14.6	29.9	36.5	13.4	04.2	—	—
MgO (%)	—	—	—	—	—	—	—	20.5
ＢＥＴ法								
比表面積 m^2/g	642	453	500	372	521	103	714	630
細孔容積 ml/g	0.63	0.47	0.63	0.55	0.56	0.22	0.7	0.53
細孔径 (Å)	39	41	50	59	43	85	39	33
Hg法								
8～1000(Å)	0.30	0.22	0.28	0.44	0.55	0.37	0.37	0.32
50～1000(Å)	0.04	0.05	0.08	0.16	0.35	0.09	0.05	0.05
見掛比重g/ml	0.61	0.62	0.57	0.48	0.62	0.58	0.54	0.5
吸油量ml/100g	80	66	64	80	66	84	100	104
粒径 (μm)	6.2	4.2	3.8	3.8	5.2	5.5	6.2	5.0
SEM法による粒径 (μm)	4-7	2-4	2-4	2-4	3~5	3-5	4-7	3-5
磁力試験 (g)	0.06	0.12	0.14	0.16	0.12	0.18	0	0

【００５９】

【発明の効果】本発明によれば、ケイ酸アルカリ水溶液、磁性体粒子、水溶性重合体及び部分中和量の酸を混合放置し、生成する粒状物を分離後中和することにより、磁性体非晶質シリカ複合粒子が容易に得られ、この複合粒子は、非晶質シリカのマトリックスと、このマトリックス中に分散した磁性体粒子とからなるという特徴を有する。即ち、この複合粒子では、粒子の表面も粒子の内部も、非晶質シリカ及び磁性体粒子の分布が一様であり、非晶質シリカの種々の特性、例えば吸着性、水分吸着性、充填剤機能、担体機能等と、磁性体としての磁気的特性とが有効に発現される。

【図面の簡単な説明】

【図１】実施例１で得られた磁性体非晶質シリカ複合粒子のＸ線反射電子像を示す電子顕微鏡写真である（倍率５，０００倍）。

【図２】実施例１で得られた磁性体非晶質シリカ複合粒子のＸ線二次電子像を示す電子顕微鏡写真である（倍率５，０００倍）。

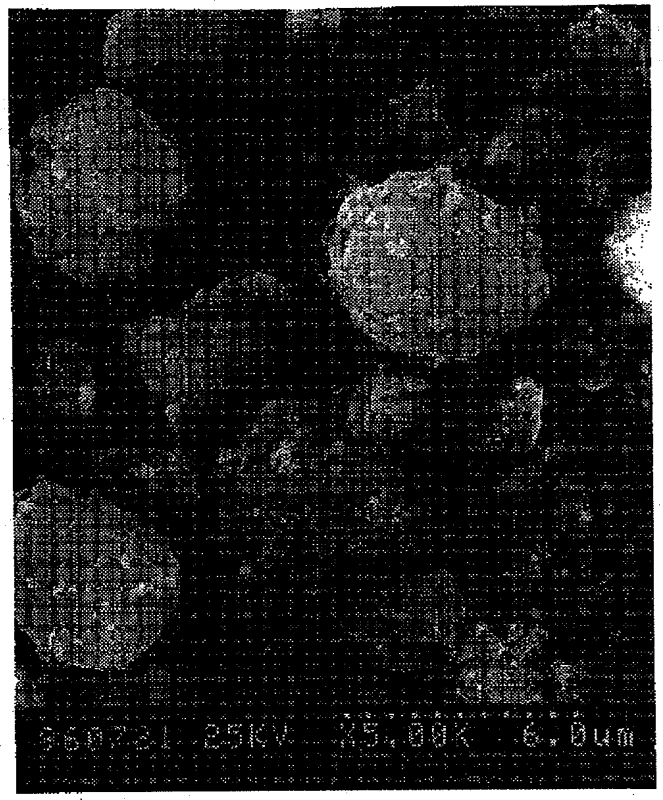
【図３】各実施例で得られた磁性体非晶質シリカ複合粒子の比表面積とフェライト含有率の関係を示す図である。

【図４】各実施例で得られた磁性体非晶質シリカ複合粒子の細孔容積とフェライト含有率の関係を示す図である。

【図５】実施例１で得られた磁性体非晶質シリカ複合粒子のコールターカウンター法による粒度分布図である。

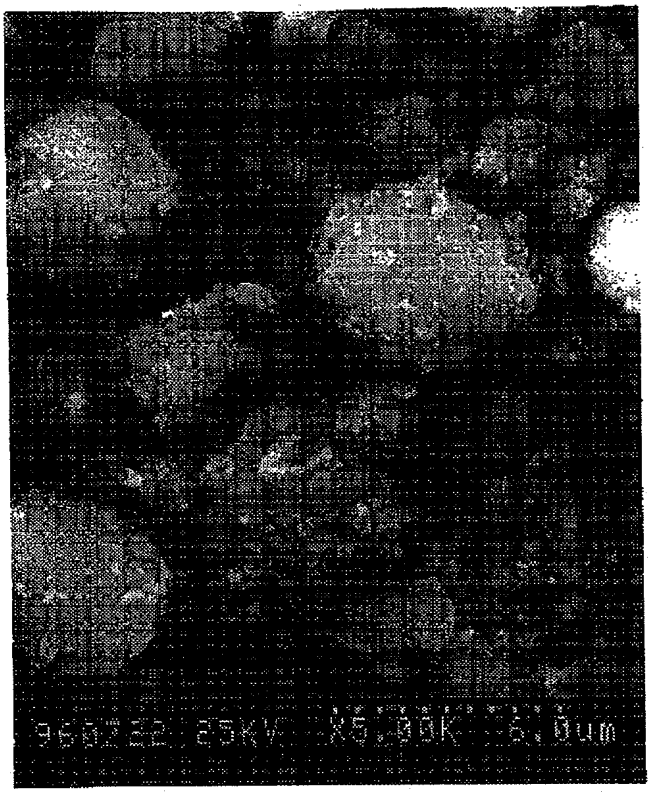
【図１】

図面代用写真

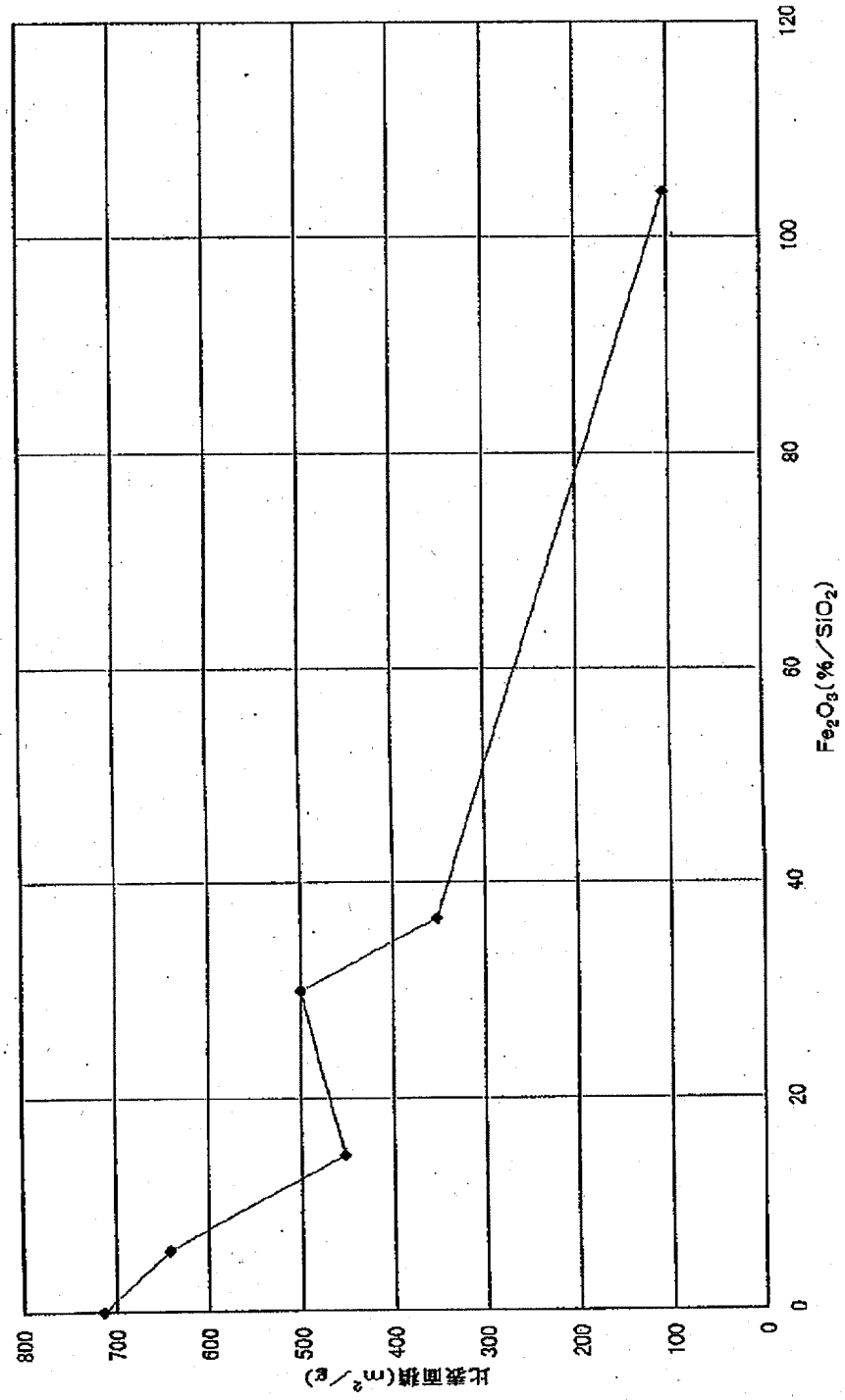


【図２】

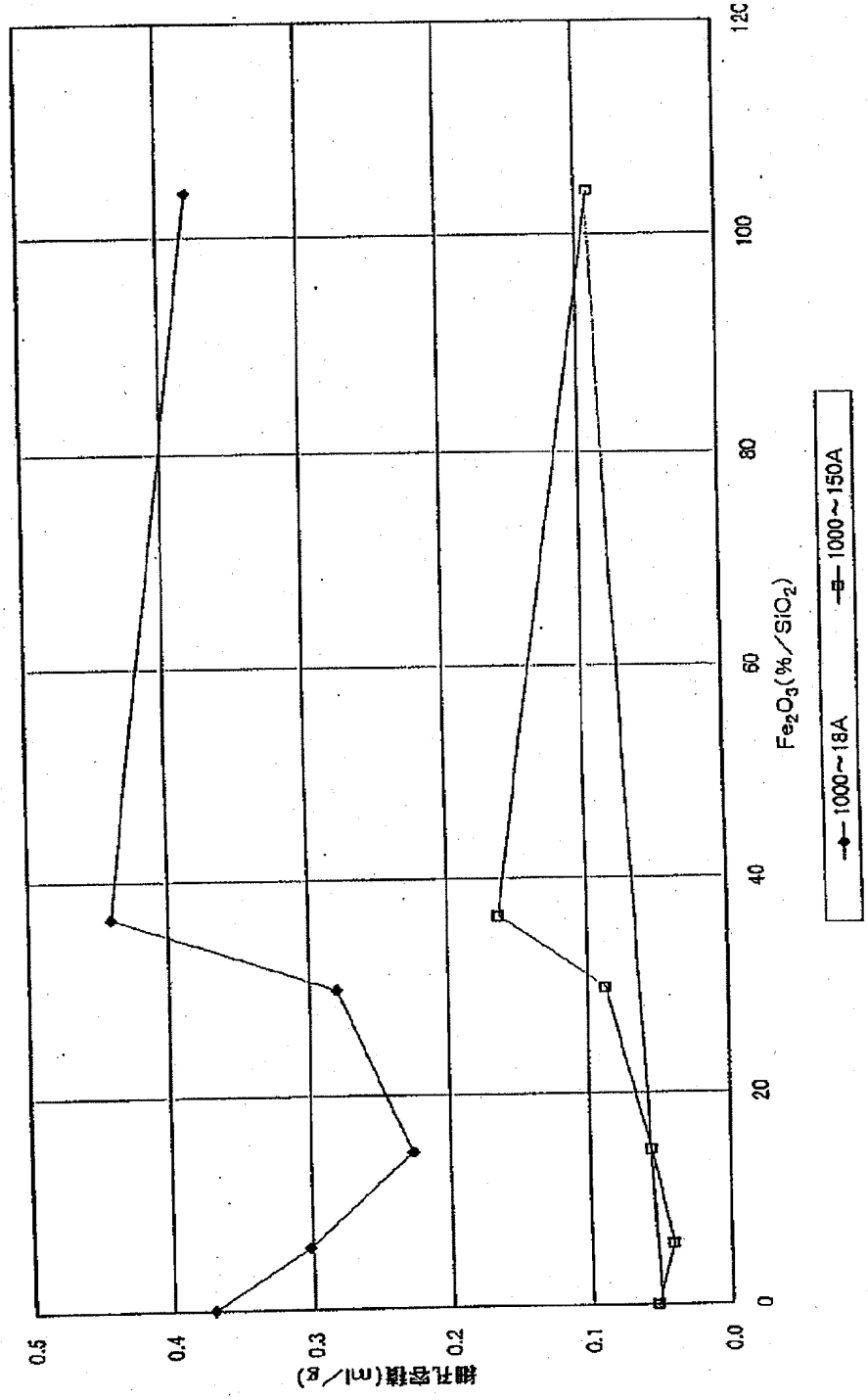
図面代用写真



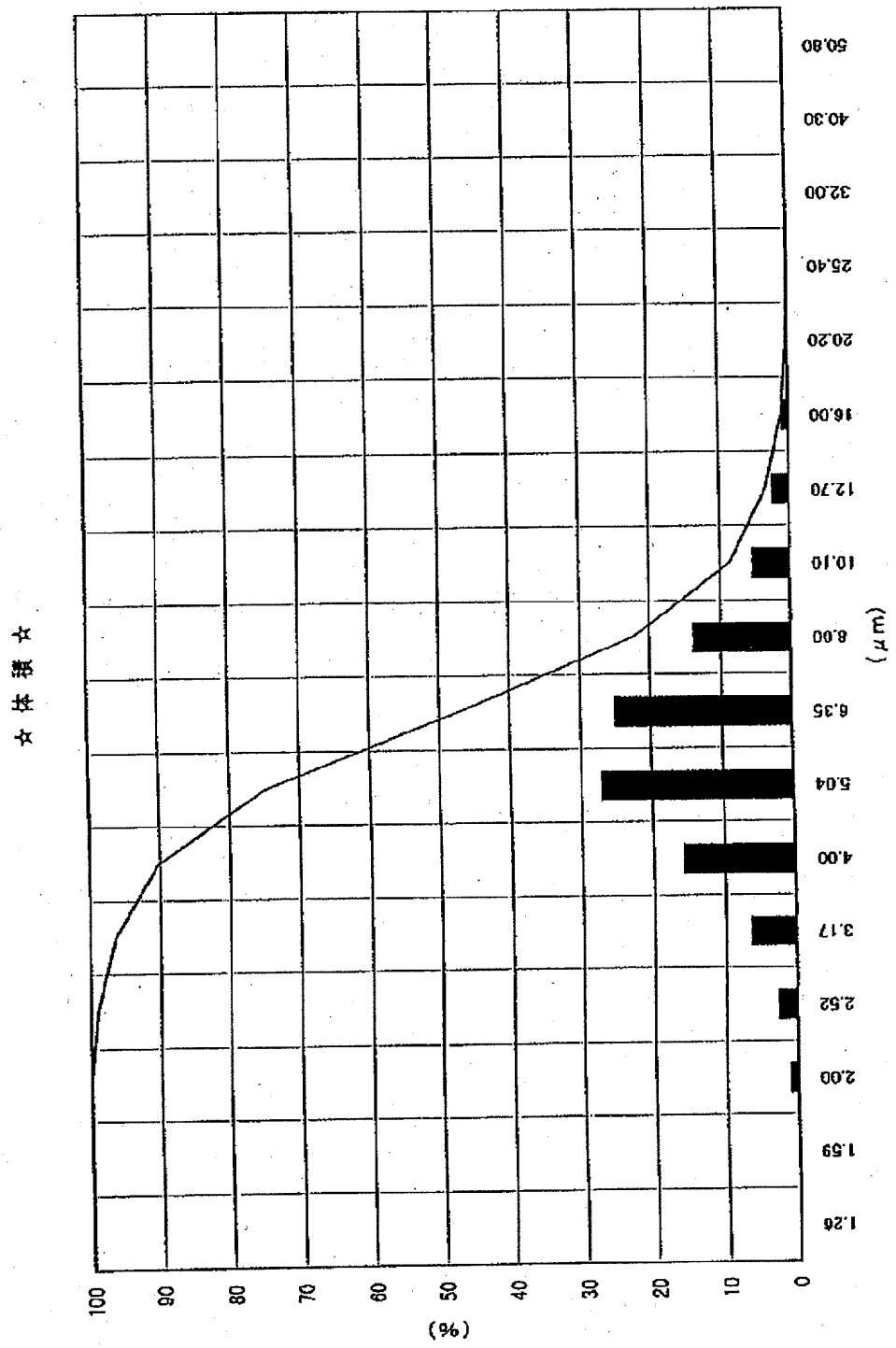
【図３】


比表面積(m²/g)
800
700
600
500
400
300
200
100
0
120
100
80
60
40
20
0
Fe2O3(%/SiO2)

【図４】


細孔容積(ml/g)
0.0
0.1
0.2
0.3
0.4
0.5
0
20
40
60
80
100
120
Fe_2O_3(%/SiO_2)
1000~18A
1000~150A

【図５】


☆体積☆
100
90
80
70
60
50
40
30
20
10
0
(%)
50.80
40.30
32.00
25.40
20.20
16.00
12.70
10.10
8.00
6.35
5.04
4.00
3.17
2.52
2.00
1.59
1.26
(μm)